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Assessment of Emerging Technologies for Metal Finishing Pollution Control: Three Case Studies

CENTEC Corp.
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This research program was initiated with the objective of bringing information concerning performance and cost of new wastewater treatment technologies to the attention of the metal finishing community.

Many novel approaches to treatment of electroplating wastewater have been evaluated based on available information under an earlier effort. The most promising of these were selected for further investigation to include sampling, performance verification, and cost analysis. This report presents the results of that investigation for the three emerging technologies selected.

The treatment methods included a system for treatment of electroplating wastes with ozone, a technique for chrome recovery by ion transfer, and a method of treating mixed wastestreams using ion exchange. Performance of each of these technologies was evaluated through sampling and analysis of prototype operation under normal production conditions. Performance data and cost projections for each system are presented herein.

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Three Case Studies

by

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Contract No. 68-03-2907-09

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes an investigation of three promising new technologies for metal finishing wastewater pollution control. Each of the systems presented here was characterized while in prototype operation under production conditions. Performance and cost data are given. This information should assist metal finishers in their evaluation of the many competing pollution control alternatives. For additional information, please contact the Nonferrous Metals and Minerals Branch.

David G. Stephan

Director

Industrial Environmental Research

Laboratory, EPA, Cincinnati, Ohio

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The treatment methods studied included a system for treatment of electroplating wastes with ozone, a technique for chrome recovery by ion transfer, and a method of treating mixed wastestreams using ion exchange. Performance of each of these technologies was evaluated through sampling and analysis of prototype operation under normal production conditions. Performance data and cost projections for each system are presented herein.

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SECTION 1

INTRODUCTION

The past decade of environmental concern has resulted in legislation aimed at reducing the amounts of industrial wastes entering the nation's waterways. In 1972, the Federal Water Pollution Control Act (PL 92-500) provided a mandate for controlling industrial wastewater discharges to receiving streams or Publicly Owned Treatment Works (POTW's). Later laws were more specific in nature such as the Clean Water Act Amendments of 1977 (PL 95-217) which emphasized control of toxic pollutants such as cyanide, chromium, nickel, cadmium, zinc, and lead. Even more recently, The Resource Conservation and Recovery Act (PL 94-580) has set limitations on industry that encourage recovery of raw materials from wastestreams rather than their discharge and disposal.

National pretreatment limitations recently promulgated for electroplaters discharging to POTW's are presented in Table 1. It should be remembered that states and/or municipalities may require more stringent regulations than these Federal guidelines.

Economics also play a role in the trend toward technologies with the potential for resource recovery and reuse rather than "destructive" conventional technologies. Table 2 shows the rise in cost of plating chemicals, pollution control chemicals, and utilities from 1972 to 1980. The sharpest increases have occurred in common plating chemicals, some of which have risen in cost over 200 percent in less than a decade.

These two factors have forced electroplaters to reevaluate their production processes and treatment methods. In-plant changes, improved treatment schemes, and water use reduction methods all have the potential to reduce the impact of increased environmental protection regulation and rising costs. As a result there is a continued interest in alternative techniques which can achieve the intent of environmental legislation and reduce operating costs incurred by the electroplater.

TABLE 1. PRETREATMENT STANDARDS FOR EXISTING SOURCES: SUBPARTS A, B, AND D-H[a]

Pollutant	Pretreatment Standard (mg/l) Daily Maximum	4-d Average
Plants discharging <10,000 gal/d:		
Cyanide, amenable	5.0	2.7
Lead	0.6	0.4
Cadmium	1.2	0.7
Plants discharging >10,000 gal/d		
Cyanide, total	1.9	1.0
Copper	4.5	2.7
Nickel	4.1	2.6
Chromium	7.0	4.0
Zinc	4.2	2.6
Lead	0.6	0.4
Cadmium	1.2	0.7
Silver[b]	1.2	0.7
All metals	10.5	6.8

[a]See table below.
[b]Applies only to Subpart B.

SOURCES: U.S. Environmental Protection Agency, "Effluent Guidelines and Standards: Electroplating Point Source Category; Pretreatment Standards for Existing Sources," Federal Register 44(175):52590-52629, Sept. 7, 1979. U.S. Environmental Protection Agency, "Effluent Guidelines and Standards, Electroplating Point Source Category, Pretreatment Standards for Existing Sources," Federal Register 44(191): 56330-56333, Oct. 1, 1979. U.S. Environmental Protection Agency, "Effluent Guidelines and Standards, Electroplating Point Source Category, Pretreatment Standards for Existing Sources; Correction," Federal Register 45(59):19245-19246, Mar. 25, 1980. U.S. Environmental Protection Agency, "Electroplating Point Source Category, Effluent Guidelines and Standards, Pretreatment Standards for Existing Sources," Federal Register, in preparation, 1980.

(continued)

TABLE 1 (continued)

EPA Classification of Electroplating Industry

Subpart	Description
A	Electroplating of common metals (Al, Cd, Cu, Cr, Fe, Ni, Sn, Pb, Zn, and any combination)
B	Electroplating of precious metals (Au, In, Pt, Rh, and Ag)
C	Electroplating of specialty metals
D	Anodizing (anodizing, acid cleaning, and alkaline cleaning)
E	Coatings (coloring, chromating, phosphating, stripping, immersion plating, acid cleaning, and alkaline cleaning)
F	Chemical etching and milling (chemical milling, etching, bright dipping, acid cleaning, and alkaline cleaning)
G	Electroless plating
H	Printed circuit board manufacturing

Note: Subparts A, B, and C may involve stripping, coloring, phosphating, acid cleaning, and alkaline cleaning.

TABLE 2. RAW MATERIAL, POLLUTANT CONTROL CHEMICALS, AND UTILITIES USED BY THE ELECTROPLATING INDUSTRY

Item	1972 Cost	1980 Cost
Plating chemicals ($/lb):[a,b]		
Boric acid (H_3BO_3)	0.069	0.224
Cadmium chloride ($CdCl_2$)[c]	-	2.82
Chromic acid (H_2CrO_4)[c]	0.37	1.03
Copper cyanide ($Cu(CN)_2$)[c]	1.05	2.62
Copper sulfate ($CuSO_4$)[c]	0.47	0.89
Nickel chloride ($NiCl_2$)[c]	0.67	1.35
Nickel sulfate ($NiSO_4$)[c]	0.50	1.03
Sodium cyanide (NaCN)[c]	0.21	0.48
Zinc (as Zn metal)[c]	0.18	0.39
Zinc cyanide ($Zn(CN)_2$)[c]	0.64	2.14
Water pollution control chemicals ($/lb):[a,b]		
Calcium hydroxide ($Ca(OH)_2$)	0.010	0.17
Calcium oxide (CaO) quicklime	0.009	0.16
Chlorine (Cl_2)	0.038	0.075
Ferrous sulfide (FeS)	-	0.40
Hydrochloric acid (28% HCl)	0.0135	0.30
Sodium bisulfite ($NaHSO_3$)	0.066	0.21
Sodium carbonate (58% Na_2CO_3)	0.018	0.05
Sodium hydroxide (98% NaOH equiv.)	0.036	0.17
Sodium hypochlorite (NaOCl)	-	0.40
Sodium sulfide (Na_2S)	0.07	0.14
Sulfur dioxide (SO_2)	0.038	0.14
Sulfuric acid (H_2SO_4)	0.017	0.41
Utilities:[d]		
Electricity ($/kWh)	0.028	0.05
Steam by energy source ($/$10^6$ Btu):		
Natural gas	1.03	2.42
Oil	1.39	4.24
Water ($/1,000 gal):		
Use fee	0.25	0.58
Sewer fee[e]	0.25	0.72

[a]Prices are for bulk shipments of chemicals; prices for smaller quantities or especially packaged quantities may be 10 to 50 percent higher. Plating chemicals purchased with proprietary additives are from 20 to 40 percent higher.

[b]Prices from Chemical Marketing Reporter, Oct. 30, 1972, and Sept. 29, 1980.

[c]Substance is on list of EPA's 131 priority pollutants.

[d]Average prices.

[e]Typical of a metropolitan area.

The Nonferrous Metals and Minerals Branch of EPA's Office of Research and Development sponsored a search for emerging technologies which may be able to accomplish these goals for the electroplater. This program was basically carried out in two phases. Initially, the literature and industry sources were tapped for new or novel wastewater treatment technologies. The technologies reviewed were subjected to a worth assessment which matched factors such as costs, energy consumption, effectiveness on target pollutants, and degree of applicability against conventional precipitation treatment methods. The assessment considered technologies in all stages of development. Eventually, the first phase of the project identified promising projects in three categories of development stage: already demonstrated, in a research and development stage, and in a pilot plant stage.[1]

The objective of the second phase of this project reported on herein is to characterize the highest ranking technologies in the already-demonstrated category by gathering performance and cost data under actual operating conditions at production metal finishing facilities. This report examines three treatment systems identified as emerging technologies of significant promise for the electroplater. The technologies are presented in the form of case histories and have been evaluated with respect to their capability to reliably remove pollutants, the initial costs of installation, and the day-to-day costs of operating the system including labor, utilities, treatment chemicals, and sludge disposal.

The systems under consideration here were each sampled over 4 or 5 consecutive days of operation under normal production conditions. Four grab samples of influent and effluent of the system were collected over the production day at each plant for specific pollutant parameters. In addition, samples were collected when possible prior to and following specific unit processes to establish their performance. The basic cost data presented were supplied by the manufacturers.

The systems evaluated, as selected during the earlier phase of this effort,[1] were:

- The Ozodyne treatment system
- The ChromeNapper™ chrome recovery system
- The Rinse-Loop ion exchange system

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The information presented in this report will allow electroplaters to determine if the technologies discussed are applicable to their particular needs. The wastestream characteristics presented through data gathered during the sampling period can be used for comparison to other plant wastestreams. Capital and operating cost expenditures can be estimated if the technologies described are being considered as treatment alternatives to conventional systems.

Detailed analysis of the applicability of each of these emerging technologies should be performed on a case-by-case basis, however. This is perhaps evident from the application of some of the technologies in this report. While the technology may have been successful in reducing effluent concentrations to dischargable limits, two plants, Chicago Modern and San Diego Plating, did not explore flow reduction techniques and the effect they would have on equipment sizing and costs. In addition, the application of the system at San Diego Plating, at the rinsewater concentrations and flows encountered during the sampling period, may be inappropriate in terms of minimization of costs. Nevertheless, the system as installed at San Diego Plating does have other advantages such as ease of operation and small size.

A plant must weigh all the factors involved in the selection of the proper treatment system before committing funds to such a project.

Specific conclusions with regard to each of the systems evaluated follow.

THE OZODYNE SYSTEM AT SAN DIEGO PLATING

The system exhibited reliable performance when operating on mixed wastewaters, reducing effluent concentrations of cyanide, metals, and total suspended solids to very low levels, often less than the limits of detectability.

The vacuum filter employed as part of the system was able consistently to dewater the resulting sludge to a very dry 75 percent solids content.

The system appears somewhat more expensive than conventional treatment but the low rate of sludge production will prove an important advantage as disposal costs increase.

THE CHROMENAPPER™ SYSTEM AT U.S. PLATING

The system exhibited reliable performance on a continuous unattended basis over the several days of monitoring, successfully recovering and returning to the plating tank all chrome other than that plated on the workpiece.

Very small quantities of solid waste were produced (about 1.89 liters of sludge per week), resulting in negligible sludge disposal cost.

Economic comparison with conventional evaporative recovery shows the ChromeNapper™ system to be highly attractive.

THE RINSE-LOOP SYSTEM AT CHICAGO MODERN PLATING

Although the system was plagued with operational difficulties arising from ancillary equipment, the basic ion exchange technology operated satisfactorily on the mixed wastewaters during those limited periods when it was possible to pay sufficient attention to maintenance.

Considerable operator attention was required. The system as installed at Chicago Modern Plating was operating in a shake-down mode. The system in its observed embodiment was not functioning in such a manner that its transfer to other environments can be recommended at this time.

The cost comparison with conventional technology shows no advantage for the Rinse-Loop system. However, the ability to achieve consistent operation with less operator attention would change that conclusion.

SECTION 3

TREATMENT OF ELECTROPLATING WASTES WITH OZONE

INTRODUCTION

To reduce cyanide concentrations in the effluent from electroplating shops, chlorine gas or sodium hypochlorite is used to oxidize the highly toxic cyanide to cyanate, then to bicarbonates and nitrogen. The typical reaction using chlorine is, in the first stage:

$$NaCN + 2NaOH + Cl_2 \longrightarrow NaCNO + 2NaCl + H_2O$$

and in the second stage:

$$2NaCNO + 5NaOH + 3Cl_2 \longrightarrow 6NaCl + CO_2 + NaHCO_3 + N_2 + 2H_2O$$

References are available to describe these reactions in further detail.[2,3,4]

The conventional treatment (alkaline chlorination) is carried out in two reaction tanks connected in series. In the first tank, the pH is adjusted to between 9 and 11 using caustic or lime. The pH in the second tank is controlled to approximately 8.5 using an acidic reagent. Chlorine is added continuously to both stages. The reaction time needed is approximately 30 minutes in each stage.

Chlorine is not the only oxidant to be used for cyanide destruction. Ozone (O_3), a strong oxidant, has been used in certain applications.[2,3] The typical reaction of ozone and cyanide is described by the process of oxidation to cyanate followed by hydrolysis to carbon dioxide and ammonia.

$$CN^- + O_3 \longrightarrow CNO^- + O_2$$

$$CNO^- + 2H_2O \longrightarrow CO_2 + NH_3 + OH^-$$

The use of ozone as an oxidant, however, has been hampered by both the methods used for treatment and the nature of ozone itself.

The usual method of introducing O_3 gas into a liquid is by bubbling the gas through the liquid or by violent agitation of the gas into the liquid, or both. This technique did not provide sufficient surface area contact between the ozone and liquid molecules. Also, unless contact is immediate, the ozone quickly reverts back to oxygen. The fact that ozone is not readily dissolved in water is an additional problem. In general, these problems resulted in chlorine oxidation being the more efficient and less costly choice for cyanide destruction.

When compared to chlorine for cyanide oxidation applications, past ozone systems have not been without advantages. These include:

- o No reagent storage necessary
- o Operation is at ambient temperatures
- o Process is well suited to automatic control

THE OZODYNE SYSTEM AT SAN DIEGO PLATING

Anticipating new Federal guidelines on electroplating effluent, San Diego Plating investigated a number of treatment systems, one of which employs ozone for cyanide destruction. The San Diego Plating Company refurbishes and recycles bumpers at the rate of approximately 85 bumpers/day, 250 days/year. Nickel, chrome, copper cyanide, and iron are the principal constituents of the 45,420 liters per day discharge. The shop uses municipal water as influent and discharges to the City of San Diego POTW. The plating line has no flow restrictors and only one countercurrent rinse, the rest being single-tank overflow rinses.

The treatment system is located outside of the plating shop, the mild weather necessitating only an open-sided, covered structure. The treatment system occupies approximately 46.5 m^2. Figure 1 is a schematic of the treatment system.

No segregation of the wastestreams is practiced so mixed plating wastes are accepted in a 7570-liter holding tank. Sodium bisulfite is, however, added to the final rinse tank in the shop to reduce hexavalent chrome. These wastes are pumped to the treatment system at a flowrate typically between 68.13 and 94.6 liters per minute. The wastewaters are initially adjusted to a pH of between 10.5 and 11.5 by automatic calcium oxide (CaO) addition. The resulting calcium hydroxide reacts with the heavy metal cations in solution to form metal hydroxides which are insoluble in the alkaline environment.

This waste containing suspended heavy metal hydroxides and cyanide is then pumped to the ozone reactor system. Ozone gas under negative pressure is drawn into the waste stream with an

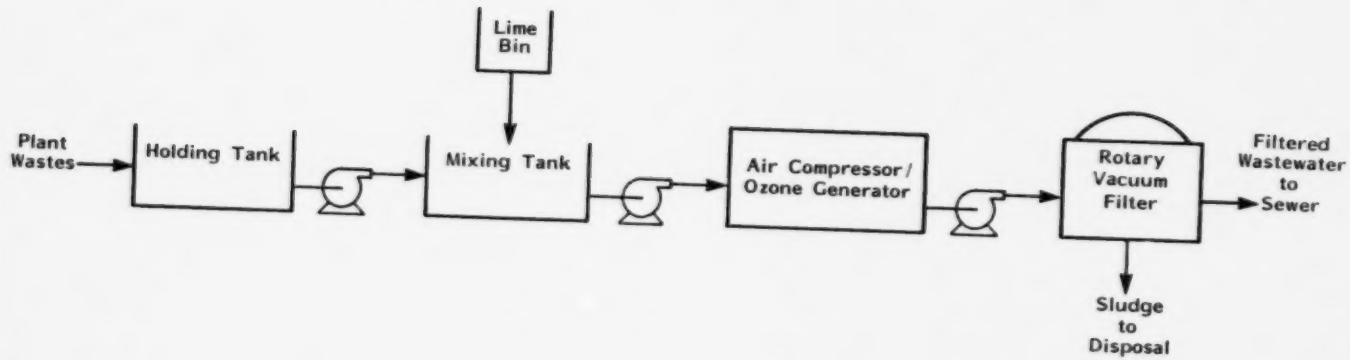

Figure 1. Diagram of treatment system at San Diego Plating

eductor. Immediately following this mixing, the wastewater containing dissolved ozone and ozone gas enters a 1136-liter ozone reactor. The wastewater is injected tangentially into the rim of a small spinning stainless steel bowl. Rim speeds can be as high as 40,000 rpm. The wastewater is shattered into a cloud or mist, thereby enormously increasing the surface area of contact between the ozone and other molecules, including cyanide. From the reactor, the wastewater is pumped to a rotary vacuum precoat filter where the wastestream is dewatered. Solids are collected for disposal while filtered effluent is sent to the sewer.

OPERATION AND PERFORMANCE

To evaluate the performance of the treatment system at San Diego Plating, effluent was monitored over a 4-day period as previously described. In addition, sampling was done at the location of the influent to the system and at specific locations before and after each treatment step. A summary of the results of the sampling program is presented in Table 3. Details of the analytical results are shown in Figures 2 through 7.

The rinsing practices at San Diego Plating, specifically the use of single overflow rinses, cause the low concentrations of metals and cyanide discovered in the treatment system influent as shown in the figures mentioned above. However, effluent concentrations of cyanide, metals, and total suspended solids were constantly reduced to very low levels, often less than the limits of detectability. The vacuum filter was also consistent in dewatering the effluent stream to approximately 75 percent solids. This outstanding performance is evidently brought about by the presence of metal oxides. Metal oxide sludge has improved dewatering characteristics and dewaters to a higher solids concentration when subjected to mechanical dewatering. This is due to the fact that metal oxide molecules are not hydrated to the same degree as are metal hydroxides. (Metal hydroxides typically have six to eight water molecules.) The waters of hydration associated with sludge solids can be removed thermally but not by mechanical means. Precipitation as metal oxide then would be expected to significantly reduce sludge volume compared with treatment of the same wastewater by hydroxide precipitation. One problem area may be the pH of the discharge. Figure 7 indicates a high pH discharge on several occasions during sampling. Adjustment of pH is not at present performed prior to discharge, but may be a necessary addition to the system.

During the sampling period, the operation of the system was without incident. About 1 hour is required by the operator for application of the filter aid, adjustment of the scraper blade

TABLE 3. SUMMARY OF SAMPLING RESULTS
SAN DIEGO PLATING

Parameter	Influent Range	Influent Average	Effluent Range	Effluent Average	Av. % Removal
Cyanide	3.75 - 0.05	1.02	0.87 - <0.02	0.08	>92.5
Total chrome	6.62 - 0.82	1.41	1.55 - 0.05	0.40	>71.6
Copper	33.0 - 5.05	9.45	1.32 - 0.04	0.05	99.5
Nickel	60.0 -10.2	20.32	0.37 - <0.10	0.13	>99.4
TSS	559 -35	135	93 - <1	11.6	>91.5
pH	12.2 - 3.4	6.4[a]	12.4 - 5.8	8.4[a]	-

[a]Median.

Average solids content of sludge = 74 percent.

Influent and effluent values, except pH, in mg/l.

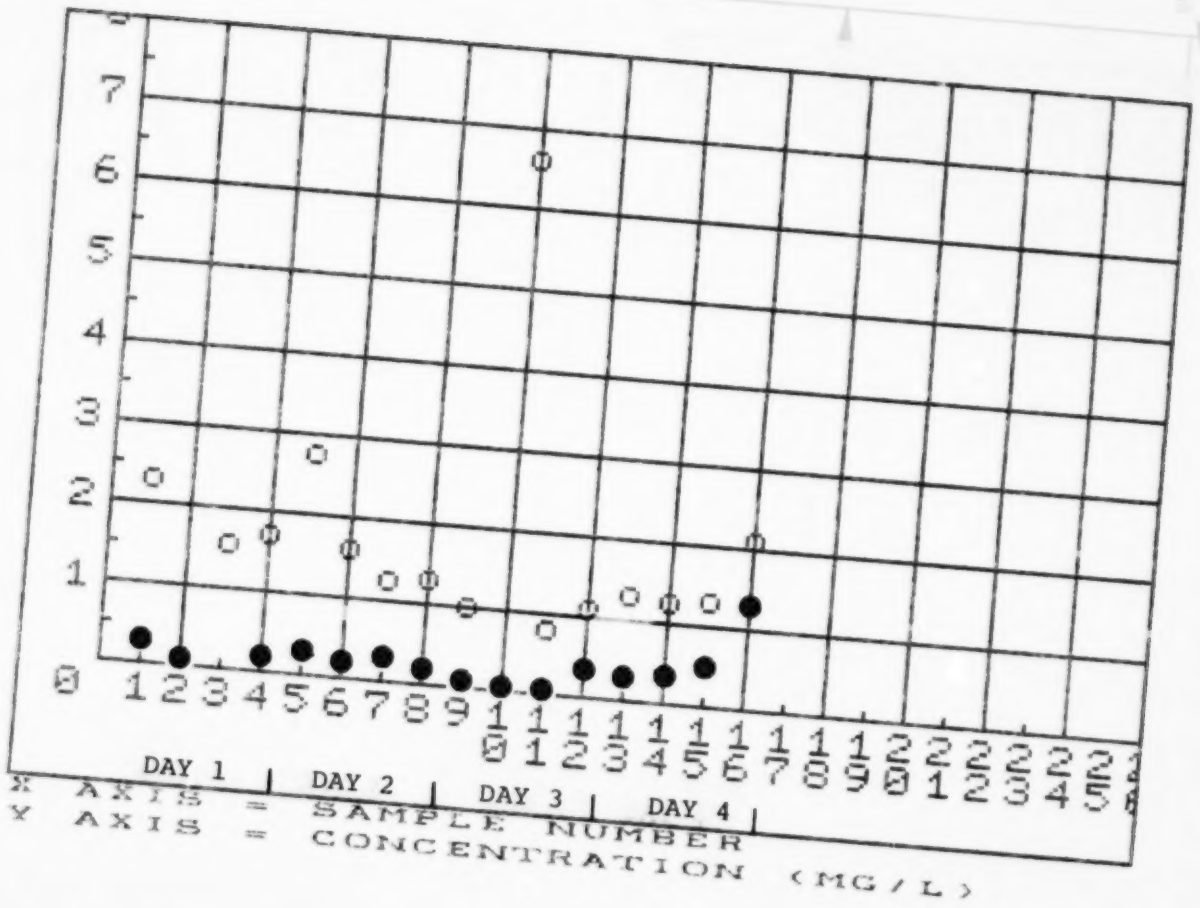

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Figure 2. San Diego Plating Ozodyne - total chrome

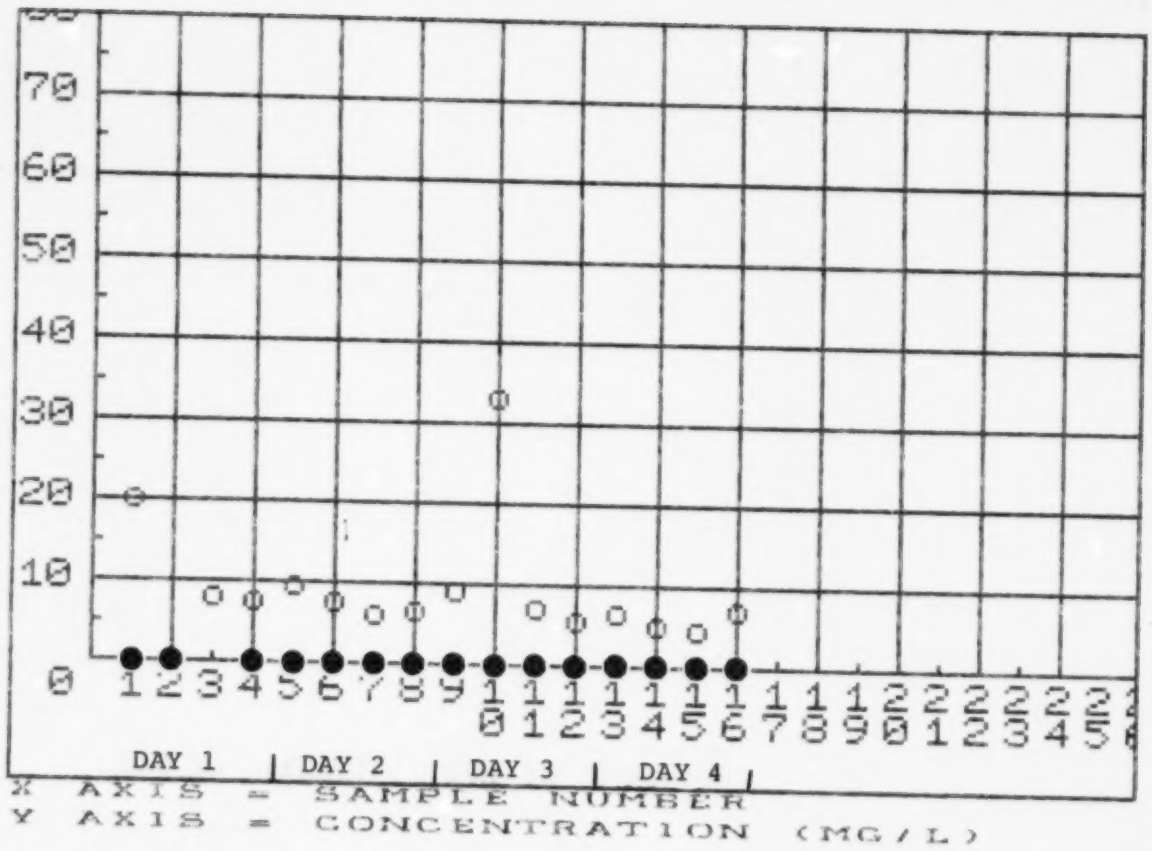

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Figure 3. San Diego Plating Ozodyne - copper

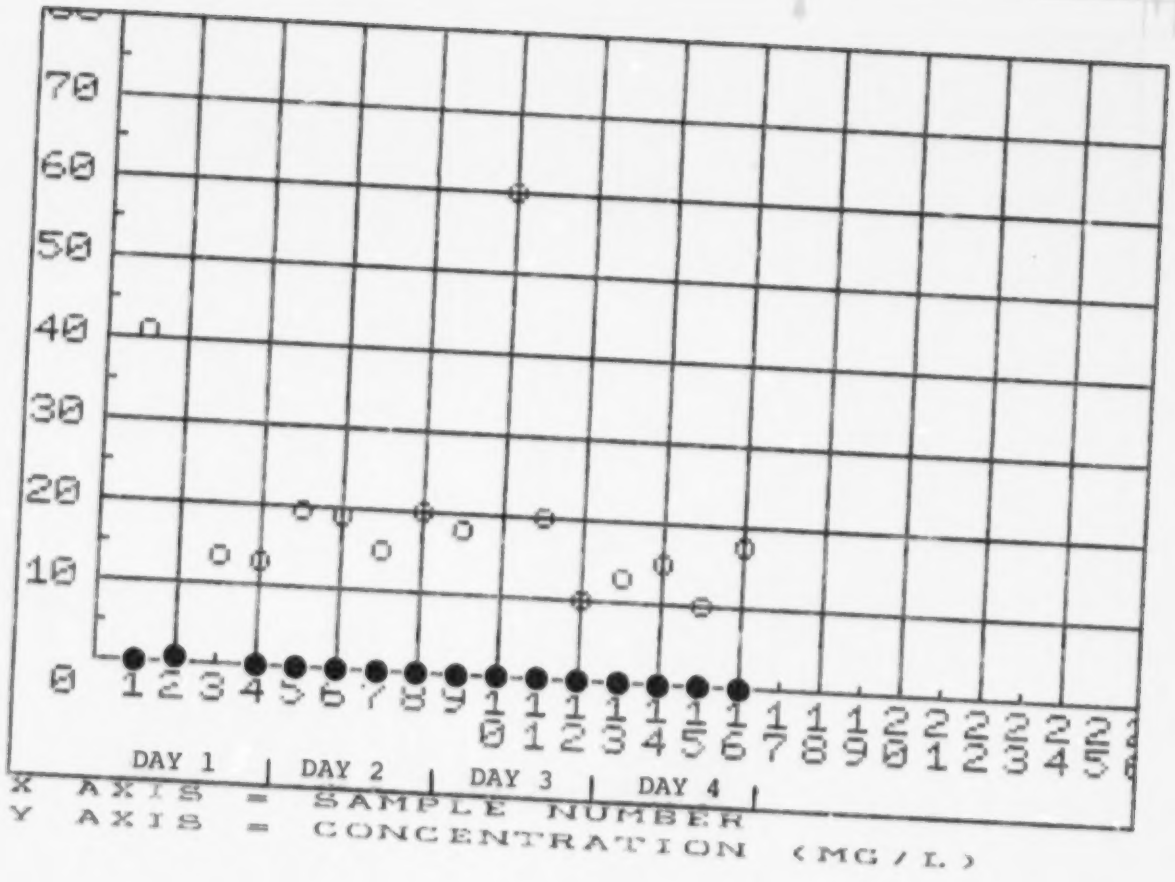

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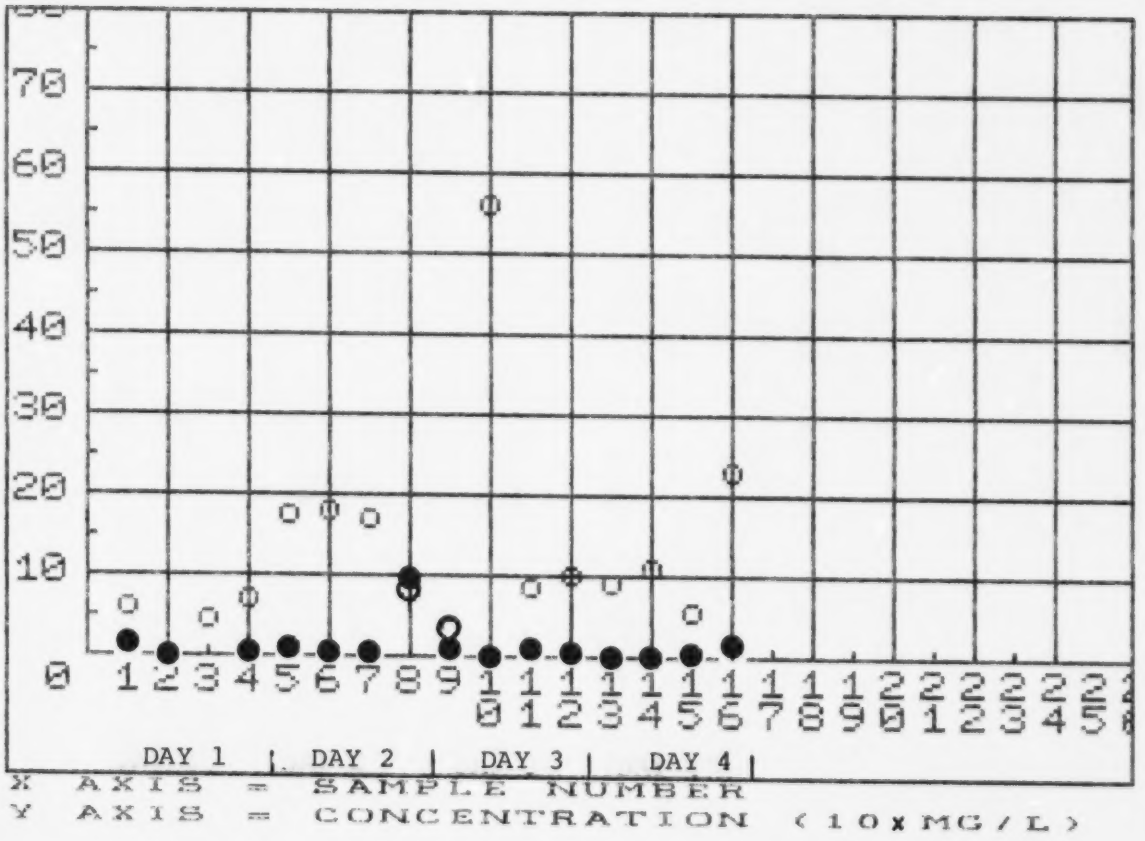
Figure 4. San Diego Plating Ozodyne - nickel



KEY: INFLUENT ○ EFFLUENT ●

Figure 5. San Diego Plating Ozodyne - total suspended solids

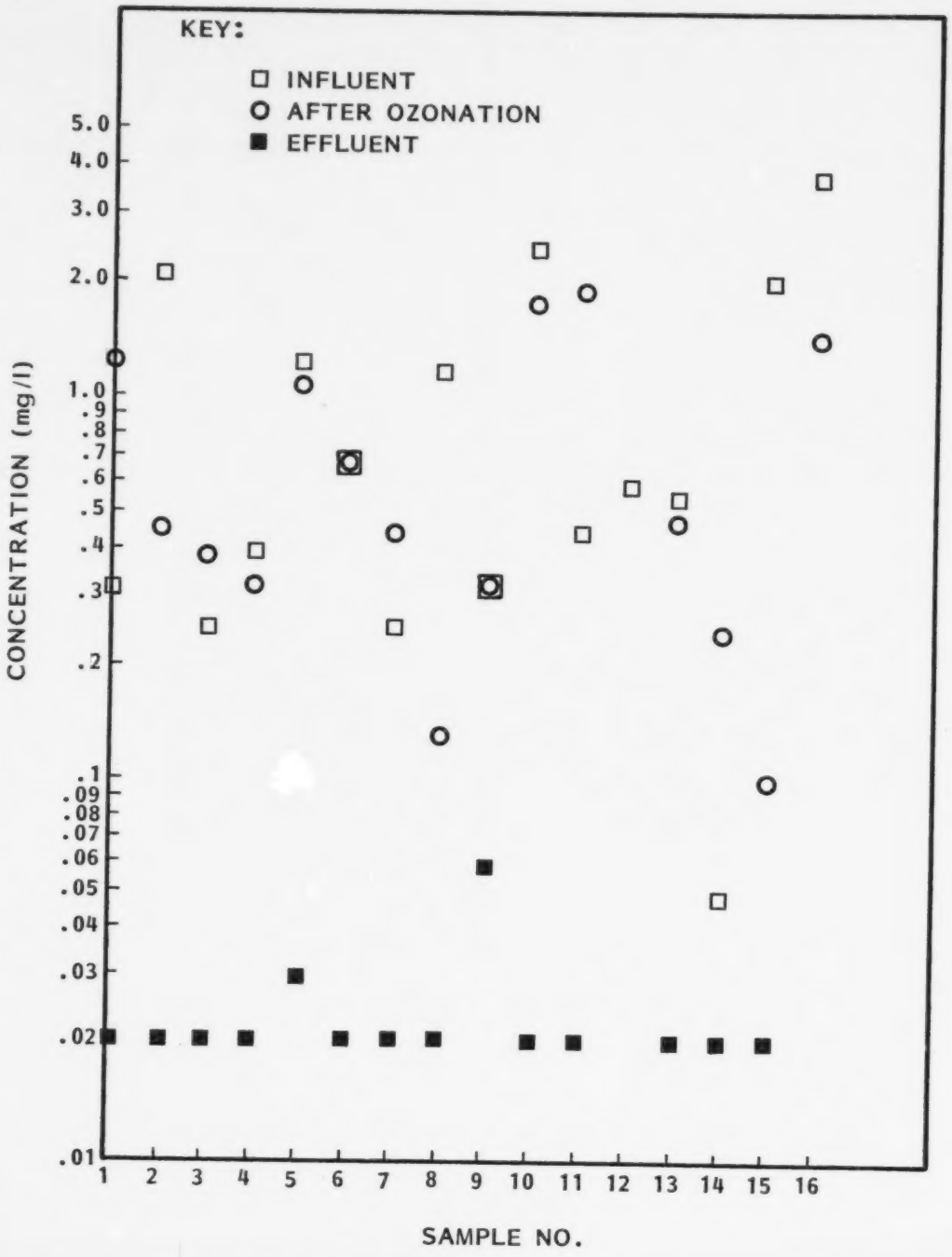
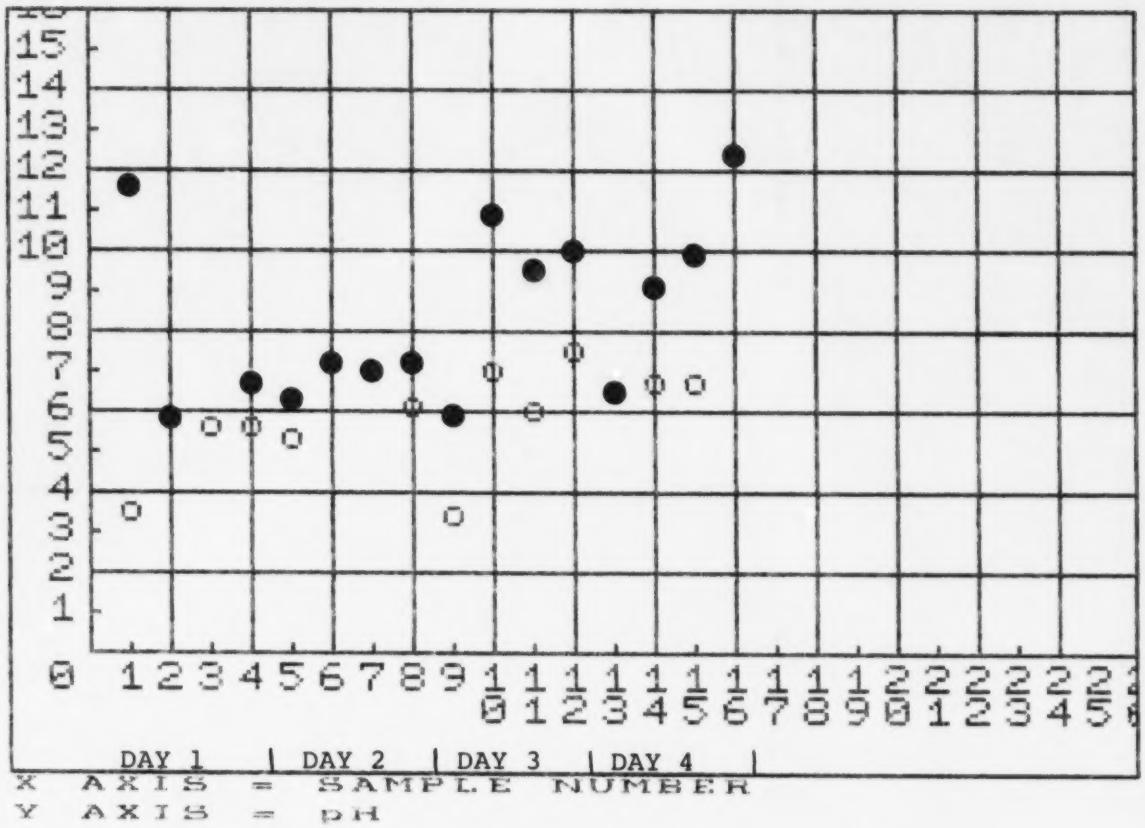


Figure 6. San Diego Plating sampling analysis results - cyanide



KEY: INFLUENT ○ EFFLUENT ●

Figure 7. San Diego Plating Ozodyne - pH

on the filter, and start-up of the air compressor and pumps. At present, solids from the filter are discharged onto a small skid and manually scooped into bags for disposal.

One anomaly shows up in Figure 6 which is believed to be associated with the analytical method used and not with the performance of the ozone system. As shown in Figure 6, some cyanide concentrations were not decreased immediately after ozonation. Even if oxidation were inefficient, an increase in cyanide concentrations could not be anticipated after this point especially in light of the low effluent concentrations. An explanation of this extends to the operation of the ozone reactor itself.

The mechanics of the contacting method used are not fully understood at this time and research is underway to examine the physics involved. The present theory is that the ions of the constituents in the wastewater are physically dissociated by the action in the reactor and do not re-form in an alkaline environment. The laboratory analysis for cyanide, however, required acidification which, at this point in the treatment system, would reassociate the ions.

In addition there is some question as to whether a cyanate is formed as a product by oxidation with ozone in this particular process. However, because of the excess $Ca(OH)_2$ which is added and the high pH at the oxidation point, calcium oxalate ($C_aC_2O_4$) is believed to be precipitated.

COSTS

Table 4 presents the annualized operating costs for the treatment system at San Diego Plating. The investment cost includes equipment and installations costs (including pumps, piping, etc.) and engineering costs.

A direct cost comparison with a conventional treatment system is not readily established. A conventional precipitation system most likely would not be designed to treat such a dilute stream as was encountered at San Diego Plating. A conventional system would rely on flow reduction and segregation of concentrated and dilute wastestreams to minimize investment and treatment cost. In addition, conventional systems are unable to concentrate solids to 75 percent as in the Ozodyne system. Even additional expenditures for filtration equipment operating on hydroxide sludge resulting from conventional treatment would achieve only 30 to 40 percent solids based on usual experience.[2] The ozone treatment system at San Diego, on the other hand, has not yet been shown to handle the more concentrated streams that could be expected from such flow reduction and segregation. The manufacturer of

TABLE 4. ANNUALIZED COST OF OZODYNE TREATMENT SYSTEM - BASED ON 4800 hr/yr OPERATION

Item	Capacity 25 GPM[a]	100 GPM
Total installed cost ($)	$200,000	$250,000
Annual operating cost ($/yr)		
Labor (4 hr/day, @ $7/hr)	8,400	8,400
Supervision	-	-
Maintenance (from manufacturer)[b]	7,000	8,750
General plant overhead	6,740	6,740
Raw materials		
Chemicals (lime, bisulfite)	1,060	4,240
Filter aid	2,450	9,800
Utilities	7,560	18,000
Sludge disposal	1,440	5,760
Subtotal	$ 33,210	$ 55,930
Annual fixed costs		
Depreciation (10% of investment)	$ 20,000	$ 25,000
Taxes & insurance (1% of investment)	2,000	2,500
Total fixed costs	$ 22,000	$ 27,500
Total annualized operating cost	$ 56,650	$ 89,190
TOTAL OPERATING COST PER HOUR	$ 11.50	$ 17.38
TOTAL OPERATING COST PER GALLON	0.0077	0.0029

[a]Configuration at San Diego Plating.

[b]Maintenance computed at 3.5 percent of investment.

the system does state that it was designed to treat expected concentrations three to four times those encountered during the sampling period. In fact, he reports that, since the sampling program described here was completed, wastewater containing metals at concentrations of 25,000 ppm was successfully treated.

To establish the basis for some comparison, however, the economics for a conventional precipitation system capable of handling the same wastestream from San Diego Plating were developed based on Reference 2. These costs are plotted on Figure 8 along with comparable data for the ozone system. For the purposes of comparison, the conventional system is assumed to include sludge dewatering equipment capable of achieving a 25 percent solids concentration. Sludge disposal costs for both systems were calculated based on a $.20/gal rate. Figure 8 indicates that the ozone system appears to be more expensive than conventional treatment systems over the range shown. This is primarily due to the high initial cost of the total system as supplied at San Diego Plating. If the ozone system is shown to be capable of handling the higher concentrations as claimed, it would become more competitive with precipitation systems. In addition, as sludge disposal costs rise in response to RCRA, the relatively low sludge production of the Ozodyne system will prove to be an important advantage.

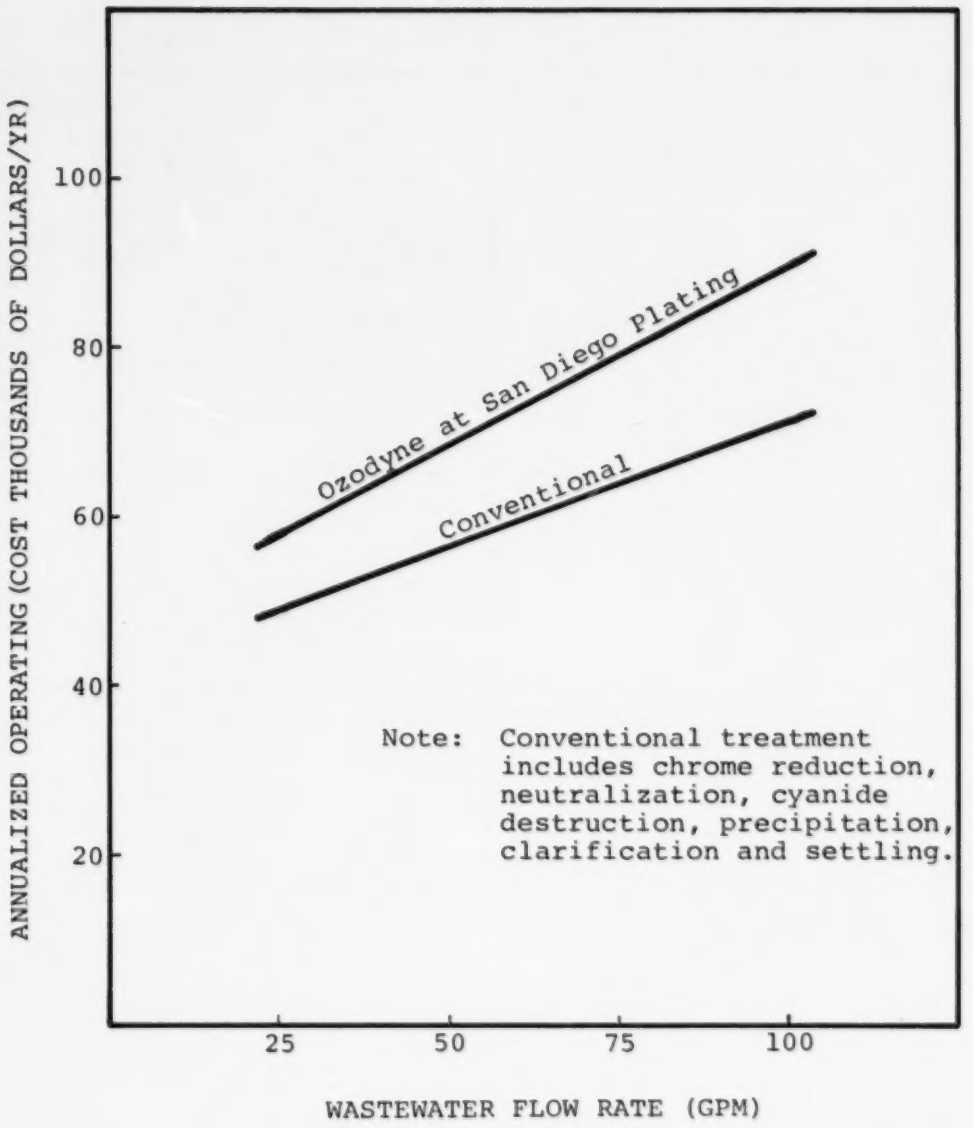


Figure 8. Annualized operating costs for conventional treatment Ozodyne treatment system at San Diego Plating

SECTION 4

CHROME RECOVERY BY ION TRANSFER

INTRODUCTION

Conventional treatment technologies rely on the reduction of the hexavalent form of chromium (Cr^{+6}) to the trivalent form (Cr^{+3}) in order that it be precipitated from a waste-stream as an insoluble hydroxide. Usually this reduction is accomplished by reaction with sulfur dioxide (SO_2) or a solution of sodium bisulfite ($NaHSO_3$).[2,3,4] The net reaction using SO_2 is:

$$3SO_2 + 2H_2CrO_4 + 3H_2O \longrightarrow Cr_2(SO_4)_3 + 5H_2O$$

The pH is maintained between 2 and 3 to speed the reaction. Electrochemical reduction is also possible with commercially available units.[2,3] This process uses consumable iron electrodes and an electrical current to reduce Cr^{+6} to Cr^{+3} as follows:

$$3Fe^{+2} + CrO_4^{-2} + 4H_2O \longrightarrow 3Fe^{+3} + Cr^{+3} + 8OH^-$$

Usually the pH is maintained such that the Fe^{+3} and Cr^{+3} ions will precipitate as hydroxides. Because ferrous ions are introduced in this process, additional solids are generated.

Since conventional and electrochemical techniques are destructive in nature and generate considerable solids as hydroxides while chrome remains a valuable raw material, methods have been developed to recover chrome from waste-streams. The first recovery systems were evaporative in design, concentrating wastewaters until high enough in chrome concentration for return to the plating bath while condensate is returned to the rinse tanks. Such systems are virtually closed loop.

No losses in plating chemicals occur other than the chrome which is plated on the workpiece. In addition, water consumption is reduced to only the water lost to surface evaporation from the plating tanks. Capital and operating costs for evaporative recovery systems are high, however. The economics depend primarily on the concentration of the rinse water being evaporated and the volume of drag-out.

More recently, work has been done in the area of electrodialysis. In electrodialysis, wastewater is passed through a series of alternating cation and anion permeable membranes. These membranes are usually impregnated with a type of ion exchange resin. An electrical potential is applied across the membranes which causes the ions to migrate to either a cathode or anode depending on their charge. Ions are then concentrated on one side of the membrane while a dilute solution is left on the other side. The concentrated stream is sent to the plating tank and the dilute stream goes to the rinse tanks.

A new electrolytic method is now available that may reduce the cost of chrome recovery. The system employs what the manufacturer calls an electrolytic ion transfer membrane. The membranes are a proprietary substance which requires no implanting of ion exchange resin as in electrodialysis membranes.

In addition, instead of using thin membranes separating three compartments in a conventional electrodialysis cell, the new system uses a single, thick (1.2 cm) ion-permeable membrane which separates two compartments. Figure 9 shows a schematic representation of a membrane module. The membrane surrounds an inner compartment approximately 3.4 liters in volume. Platinum-plated titanium anodes are inserted through the top of the module which contains the recovered chromic acid/sulfuric acid anolyte. The outside of the membrane is wrapped in a stainless steel mesh cathode. Rinsewater is the catholyte solution. Ion transfer and concentration of the chromic acid are accomplished by applying a direct current between the anodes and the mesh cathodes on the outside of each cell. Chromic acid concentrates in the anode compartment of the cell while treated dilute rinsewater is returned to the rinse tanks.

ELECTROLYTIC ION TRANSFER SYSTEM AT U.S. PLATING:
THE CHROMENAPPER™ SYSTEM

U.S. Plating specializes in refurbishing automobile bumpers. The plating line is composed of five 3,785-liter bright nickel plating tanks and one chrome plating tank. The 3,785-liter chrome tank contains chromic acid (280 g/l) and sulfuric acid (1400 mg/l). The chrome tank is followed by a three-stage countercurrent rinse (see Figure 10). Nickel, chrome, and iron are the principal metals present in their rinsewaters.

The ChromeNapper™ system at U.S. Plating is installed on the final (third) rinse. There is no discharge from the system. The first rinse tank is essentially a still rinse with a chromic acid concentration of approximately 46 g/l (23 g/l Cr). To keep this concentration steady, water from this tank is used as make-up for the chrome plating tank. The recovery

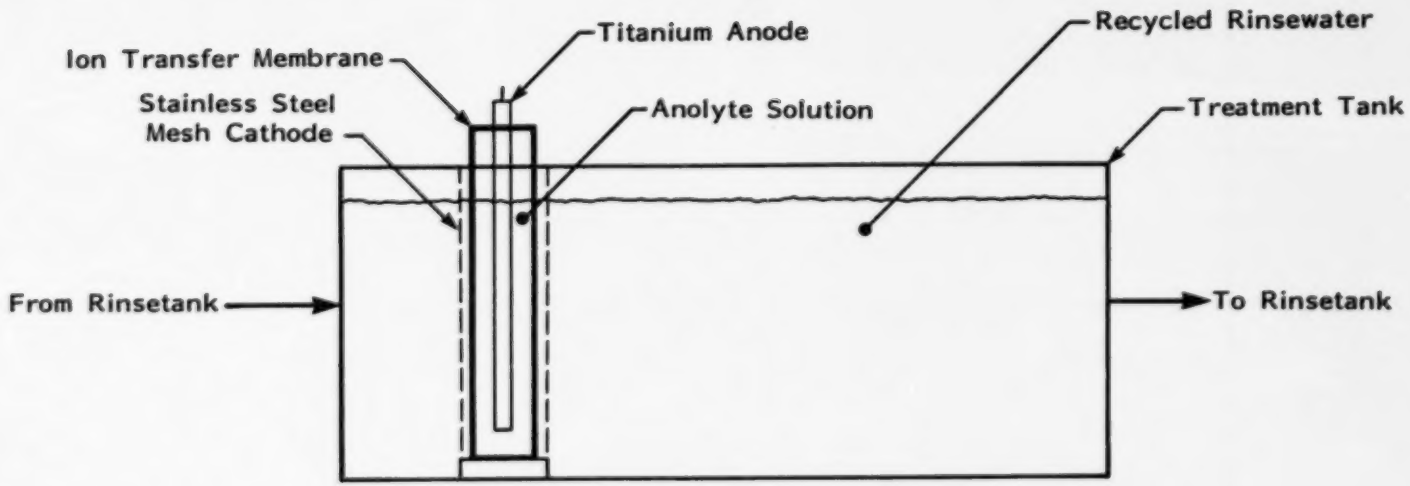


Figure 9. A membrane module - assembled

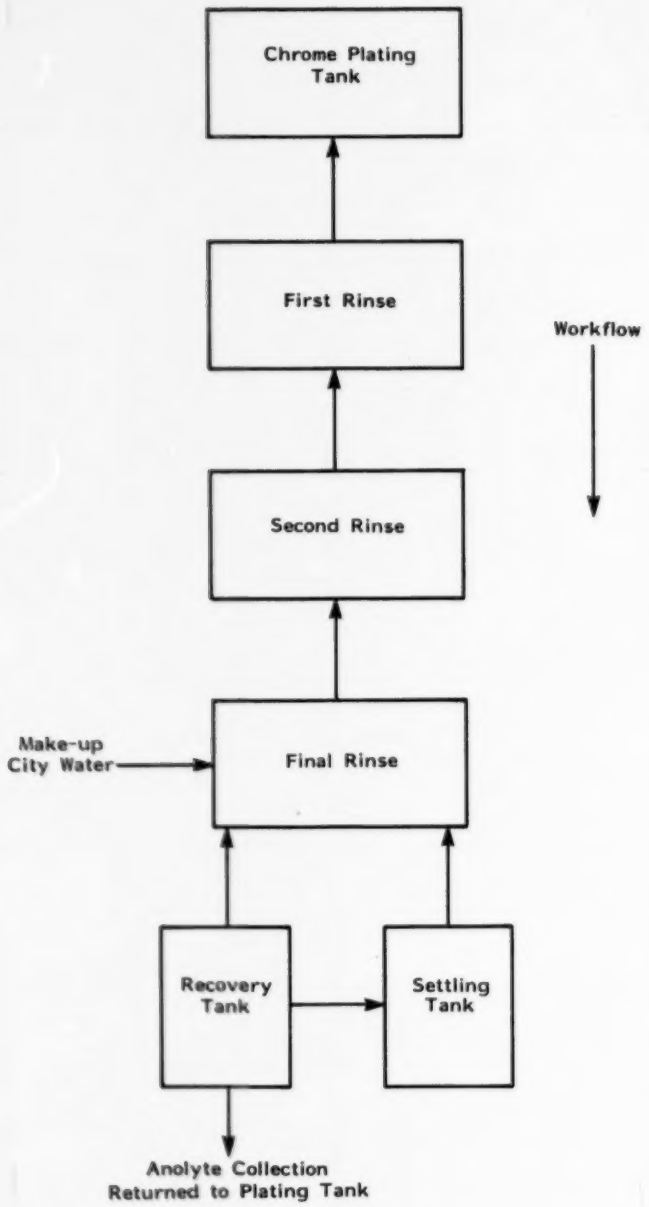


Figure 10. Chrome recovery system at U.S. Plating

system that receives rinsewater from the third rinse tank consists of a 378.5-liter tub with eight cells. The flow of rinsewater pumped through the tank is between 7.6 and 18.9 liters per minute. Direct current applied to the system typically measures about 4 amp/cell. Voltage is manually set at the rectifier, a typical value being 26 vdc. The anode attracts chromate (in which form any hexavalent chrome present exists) and sulfate ions while the cathode attracts trivalent chrome, calcium, sodium, and potassium ions. The pH of the rinsewater is approximately neutral, and hydrogen and hydroxyl ions are attracted to the electrodes. Iron, nickel, and calcium hydroxides precipitate in a second 757-liter tank which acts as a clarifier where a small amount of sludge settles out. The overflow is returned by gravity flow to the third rinse tank. Approximately 4.92 liters per hour of city water are added to the countercurrent rinse system to make up for surface evaporation.

Twice a week, chromic acid is withdrawn from the cells. At the end of the week the collected chromic acid is returned to the chrome plating tank.

OPERATION AND PERFORMANCE

The chrome recovery unit at U.S. Plating runs unattended 24 hours per day, 7 days per week, although production is only one 8-hour shift Monday through Friday. During the non-production hours and on weekends, a low current is continuously fed to the system since the electrical polarity keeps the anolyte and rinsewaters separate. Twice a week at the end of the production day, about 10 to 12 liters of anolyte are withdrawn from the cells, an operation that takes a few minutes.

Sampling was conducted over a 5-day period at U.S. Plating. A summary of the sampling results, presented in Table 5, shows the ranges of influent and effluent concentrations encountered as well as averages for the sampling period. Details of the analyses' results are shown in Figures 11 through 16. Figure 11 shows the total chrome concentrations in and out of the recovery tank. Influent to the recovery system is from the final rinse tank. Effluent from the recovery unit is returned to the final rinse. The flow rate through the ChromeNapper™ system is chosen to be such a value that the chrome concentration into and out of the unit is held nearly constant. Figure 11 shows that this is being accomplished well. Throughout each 8-hour shift (Samples 1 through 4, for example), the chrome concentration entering and exiting the unit increases as dragout from production parts contaminates the final rinse. Throughout the remaining portion of the day, the unit continues to recover chrome from the final rinse tank without interruption, so that the first sample of the next day

TABLE 5. SUMMARY OF SAMPLING RESULTS AT U.S. PLATING

Parameter	Influent to ChromeNapper™ Range	Influent to ChromeNapper™ Average	Effluent from ChromeNapper™ Range	Effluent from ChromeNapper™ Average
Total chrome	17.5 - 5.0	11.5	16.0 - 3.5	9.9
Hexavalent chrome	9.5 - 1.8	5.2	11.1 - 1.60	5.4
Nickel	4.35- 1.68	3.1	4.22- 1.78	2.9
pH	8.6 - 7.2	7.8[a]	8.6 - 7.6	8.0[a]

[a]Median.

All values, except pH, in mg/l.

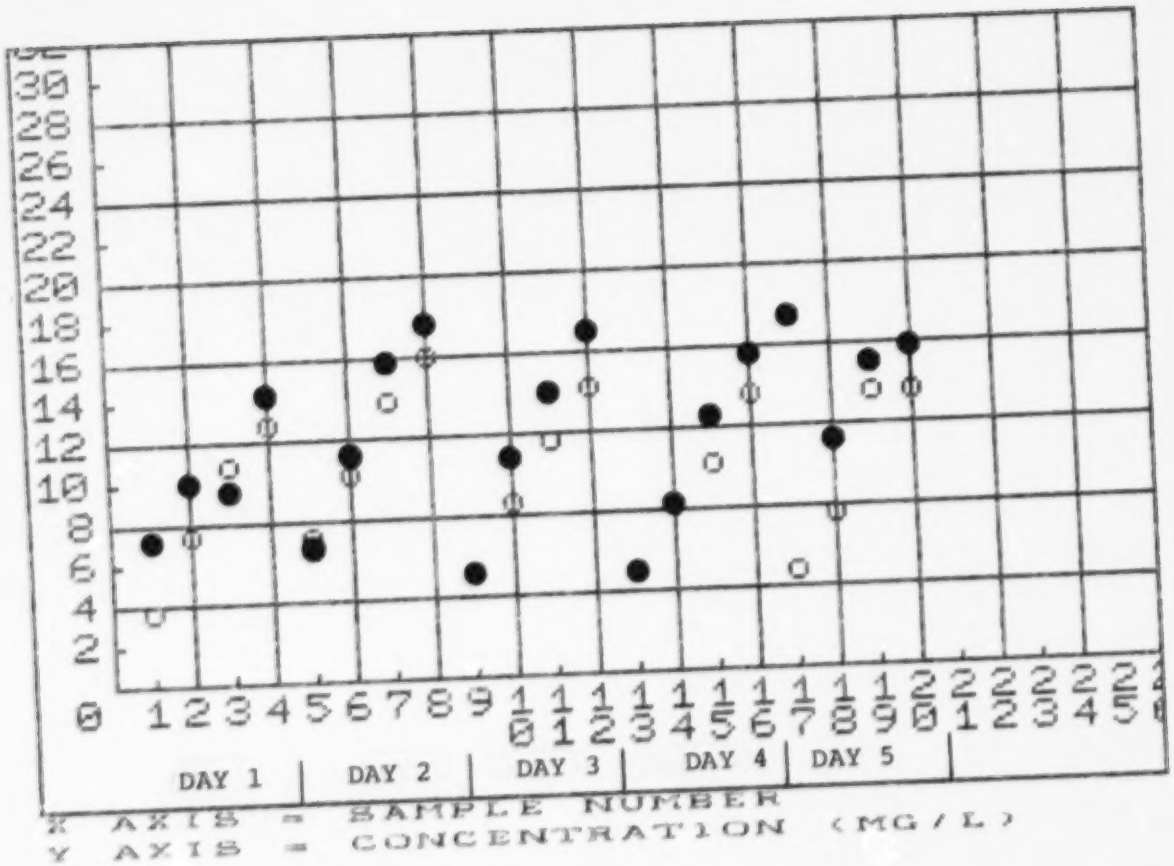


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Figure 11. U.S. Plating ChromeNapper™ total chrome - final rinse

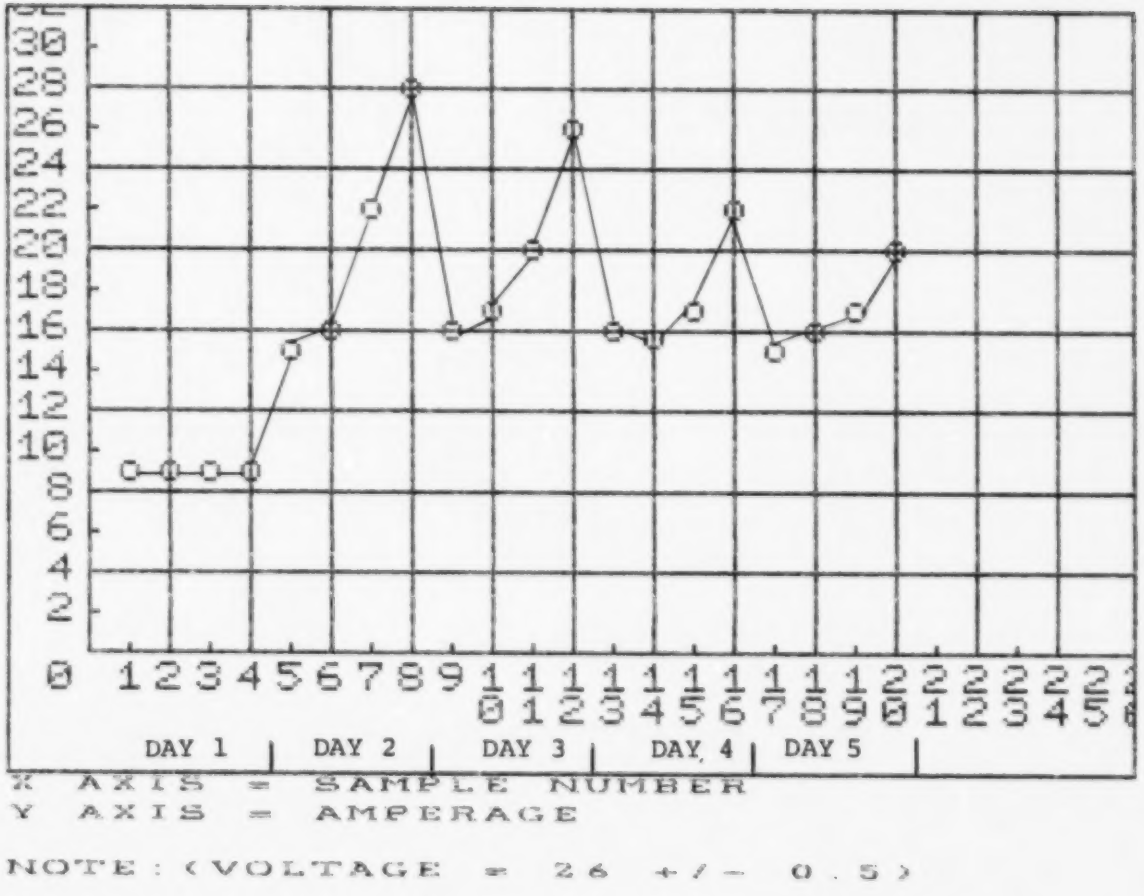

Figure 12. U.S. Plating ChromeNapper™ amperage during sampling

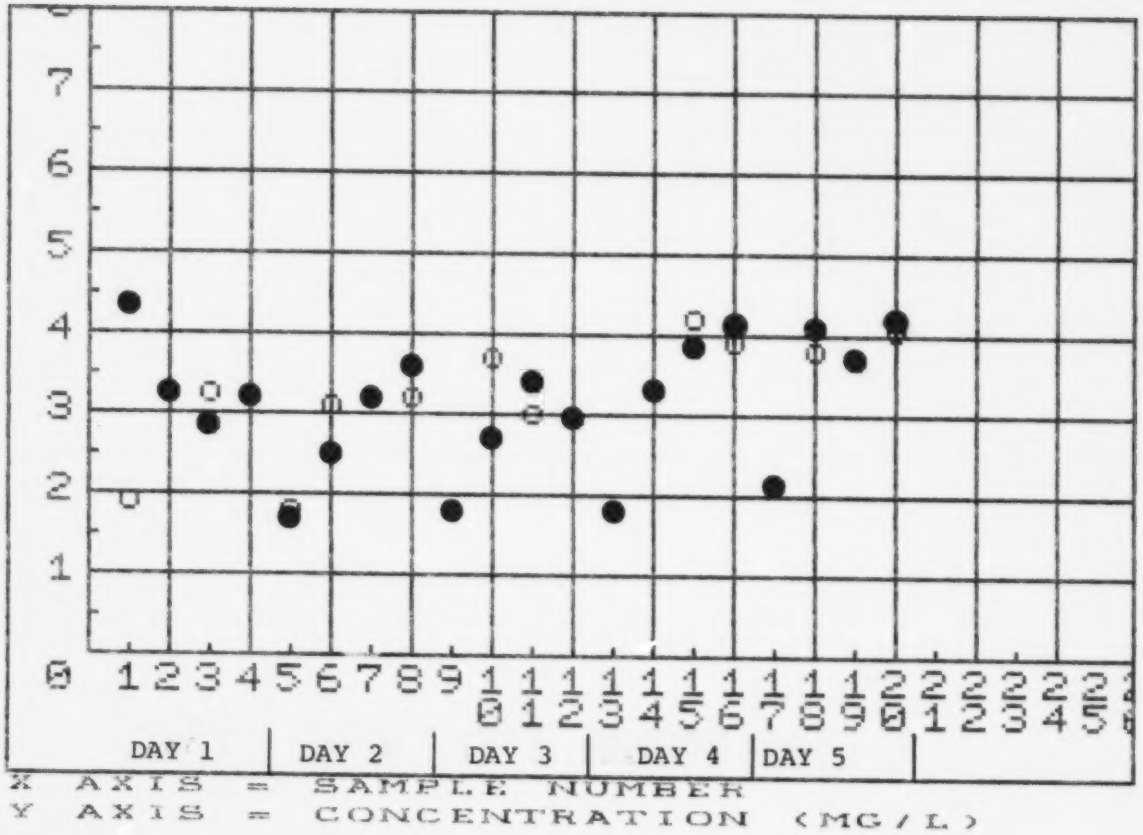

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Figure 13. U.S. Plating ChromeNapper™ final rinse tank - nickel

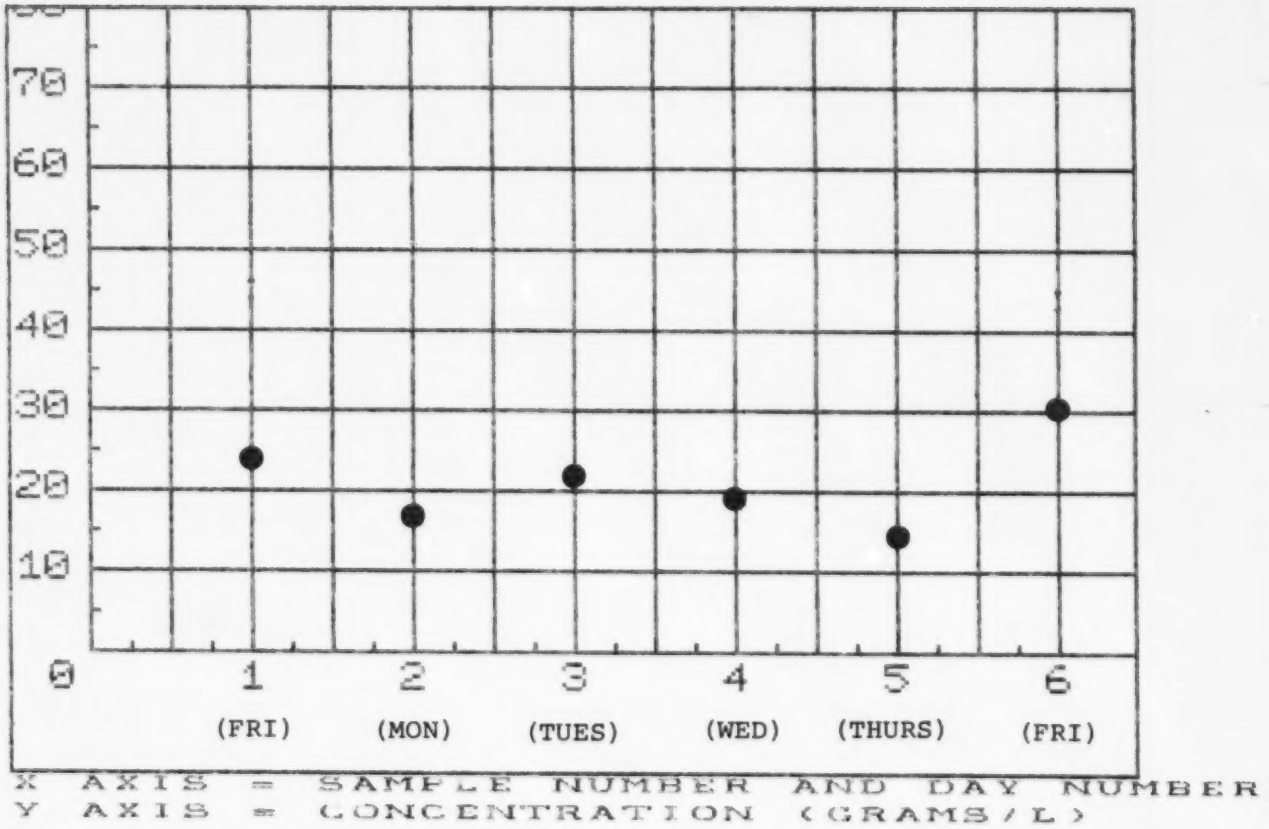

Figure 14. U.S. Plating anolyte concentration - total chrome

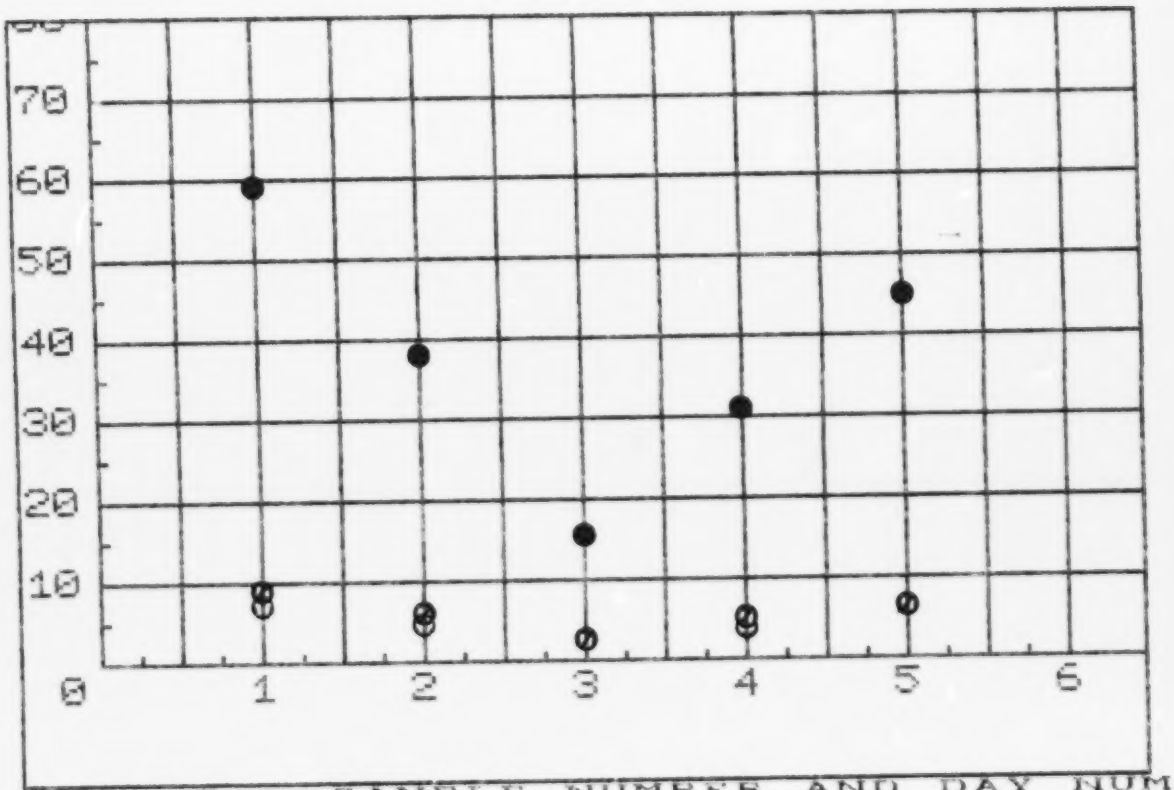

Figure 15. U.S. Plating ChromeNapper™ - sludge

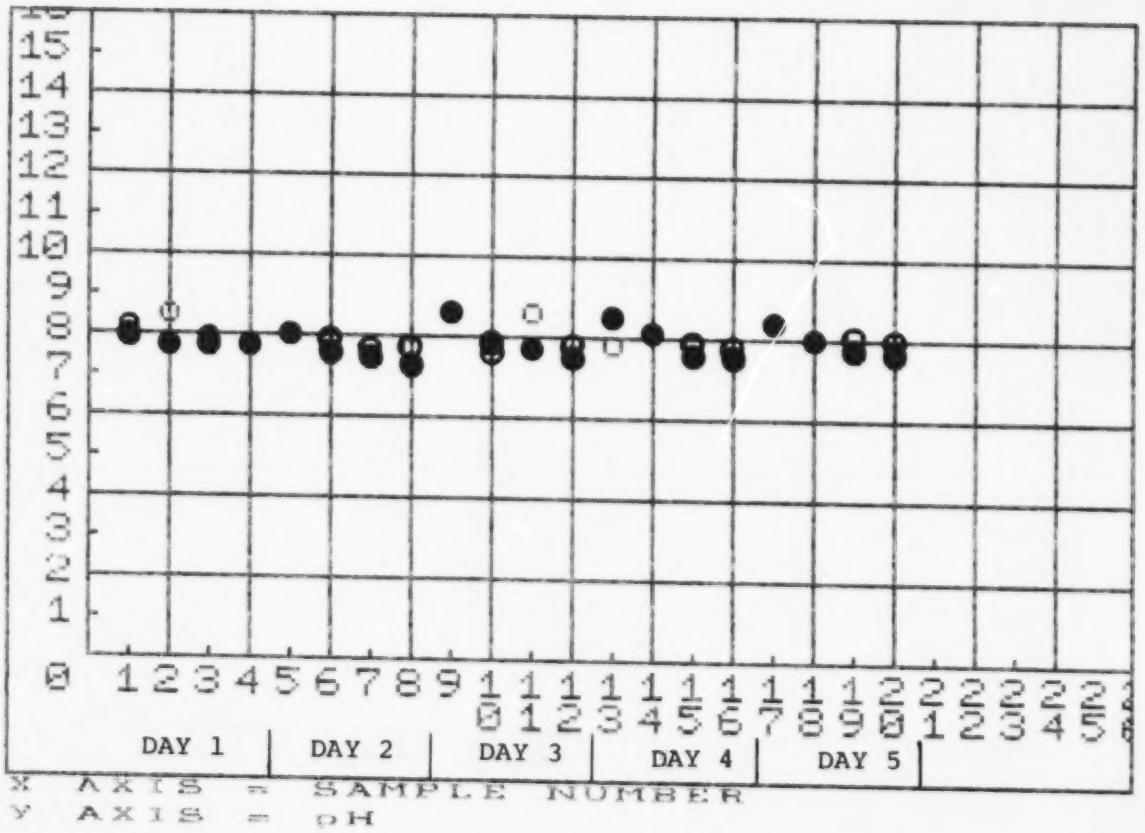

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Figure 16. U.S. Plating ChromeNapper™ - pH

(Sample 5, for instance) once again indicates a low concentration of chrome in the final rinse tank. The current, which is supplied based on the voltage set point, varies as a direct function of the concentration of chrome in the rinse tank and, as shown in Figure 12, follows the same trend as the graph of chrome concentration.

Nickel was also sampled to see if the system's performance was affected by the presence of other ions. While nickel concentrations in the rinse water generally increased during production hours, as shown in Figure 13, the concentrations observed were very low and did not appear to interfere with chrome recovery.

Anolyte concentrations of total chrome were also measured during the sampling period. Because each module holds a small volume, a single composite sample was collected over the day. As expected, the concentration of chromic acid followed the rise and fall of the average catholyte chrome concentration. The highest concentrations of chromic acid are at the end of the week as indicated in Figure 14.* Also, pH was below 1.0 in all the samples of anolyte. A very low concentration (2 mg/l) of nickel was found.

One liter underflow samples were also taken on a daily basis. The levels of metals contained in this effluent are shown in Figure 15. The level of total suspended solids in the underflow is also presented in Figure 15. Settled sludge from this source will amount to less than 113.5 liters of sludge per year. The pH remained fairly constant as shown in Figure 16.

As seen in the summary table (Table 5), the recovery system maintained an average total chrome concentration in the final rinse tank of between 11.5 and 9.9 mg/l over the 5-day sampling period. The average peak concentration reached in the effluent from the settling tank was approximately 16 mg/l, well below that originally desired (25-50 mg/l) by U.S. Plating. The manufacturers of the system report that the system installed at U.S. Plating is oversized and that a four-cell system could provide the desired concentrations.

Operation of the recovery system during the sampling period was normal and uneventful. System maintenance is reported as minimal. The cathodes may foul under certain conditions but acid cleaning is easily performed. No membrane

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*Innova Plating Waste, Ltd. reports that their analysis of the equivalent of Samples No. 1 and 6 resulted in anolyte concentrations of 44 and 45 g/l Cr^{+6} respectively.

fouling occurred during the sampling period. Membrane life has been placed at greater than 2 years based on accelerated lab tests by the manufacturer.

COSTS

The costs for the chrome recovery system at U.S. Plating are presented in Table 6 along with costs for an evaporative chrome recovery system for the chrome plating line at U.S. Plating. With the given concentrations, rinse configuration, and dragout rate at U.S. Plating, an evaporator handling 75.7 liters per hour of rinsewater was determined to be needed. This rinse rate is among the lowest for which an evaporative recovery system could be considered.

The costs for the ion transfer recovery system are for the eight-cell system at U.S. Plating. The four-cell unit suggested by the manufacturer would have a total installed cost of $13,000 which would lower annual operating costs to approximately $4,785.

The ChromeNapper™ system has a clear economic advantage. The actual advantage is even greater than indicated by Table 6 because the cost of a cation exchange column, required to control evaporator scaling in a chromic acid environment, is not included.

TABLE 6. COMPARISON OF TREATMENT COSTS[a] FOR CONVENTIONAL TREATMENT OF A CHROME WASTESTREAM AND THE CHROMENAPPER™ CHROME RECOVERY SYSTEM AT U.S. PLATING

Item	Costs	
	Evaporative[b]	Ion Transfer[c]
Total installed cost[d] ($)	$35,850	$21,000
Annual operating costs ($/yr)		
Labor	525	390
Supervision	—	—
Maintenance	2,150	1,260
General plant overhead	690	575
Raw materials		
Steam (@$4/$10^6$ Btu)	2,020	—
Cooling water (1000 gal/hr @$.58/1000 gal.)	560	—
Utilities	750	250
Replacement membranes	—	1,000
Total operating cost ($/yr)	6,695	3,475
Annual fixed costs ($/yr)		
Depreciation (10% of investment)	3,585	2,100
Taxes and insurance	360	210
Total annualized operating costs	$10,640 /yr	$ 5,785 /yr

[a] Credit for plating chemicals recovered is essentially the same for both systems as are reductions in costs for sewer fees resulting from closed-loop system.

[b] The evaporative recovery unit treats a 20 gal/hr rinse stream 2400 hrs/yr. Costs include all equipment (tanks, piping and pumps) and installation (labor, site, preparation, plumbing and electrical). Steam is assumed to be available which may not be the case at many small plating shops.

[c] Equipment costs were provided by the manufacturer. Maintenance costs and overhead costs were based on same percentages as used for the evaporative system for comparison purposes. They are probably less for the ion transfer unit since the system has few complex parts.

[d] Total installed costs include all equipment, piping and engineering. No interest on capital is included in the analysis.

SECTION 5

TREATMENT OF A MIXED WASTESTREAM BY ION EXCHANGE

INTRODUCTION

Ion exchange is a treatment method which employs inorganic and organic resin materials to remove ions (such as Cd^{+2} and CN^{-}) from wastewaters. This removal is the result of an exchange of similarly charged ions between the resin and the solution. The resins are selective in that they remove either positively charged ions (cations) or negatively charged ions (anions) from solution. Resins employed in wastewater treatment typically exchange hydrogen ions (H^{+}) for positively charged ionic compounds such as nickel, copper, and sodium, and hydroxyl ions (OH^{-}) for negatively charged sulfates, chromates, and chlorides. As the quantity of H^{+} and OH^{-} becomes equivalent, the result of this treatment is water at neutral pH and very low in dissolved solids.

After a time the resin becomes exhausted; that is, it has replaced the ions in solution with all its available, similarly charged ions. Ion exchange is a reversible reaction, however, and the resin may be regenerated. This results in small volumes of very concentrated wastewater which may be conventionally treated.

Figure 17 is an example of a typical fixed-bed ion exchange system. Initially, wastewater is passed in series through a cation column and an anion column. The cation column removes heavy metals while the anion column removes hexavalent chromium, which exists as the chromate ion.

When the upstream column's resin is exhausted, it is taken off-line and regenerated with a caustic solution. The waste stream is then routed to the other cation column. The same procedure is followed with the anion column. The anion column is regenerated with an acid solution. The spent regeneration solutions are then sent to a small conventional treatment system.

Unlike conventional treatment systems, the cost of ion exchange is independent of solution volume, making it highly efficient in terms of chemical consumption when treating

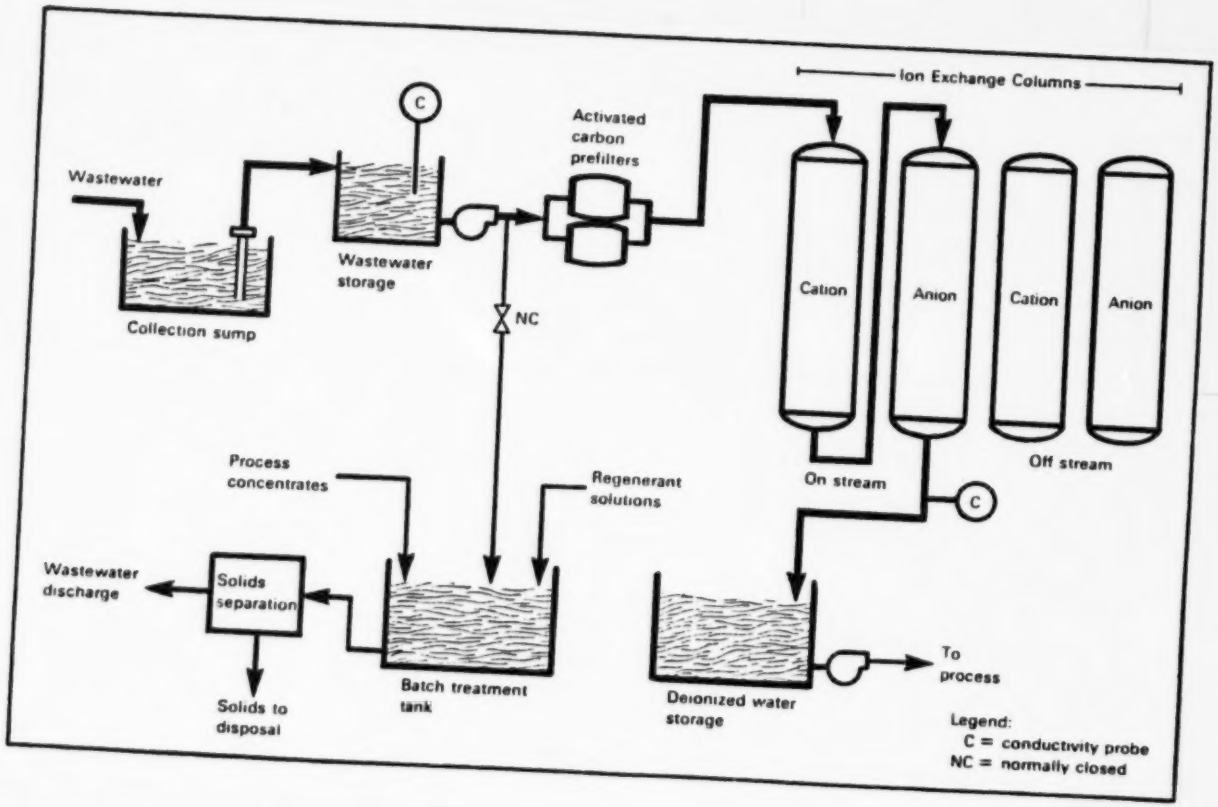

Figure 17. Ion exchange wastewater purification and recycle system

dilute concentrations of ionic contaminants. In electroplating, the greatest volume of process water is rinsewater, typically with very low concentrations of heavy metal and cyanide ions--a most attractive feature. In addition, the potential reuse of the deionized water in the rinse tanks reduces the wastestream volume requiring treatment and discharge to only the regenerant, thus greatly reducing the plant's water requirements.

ION EXCHANGE SYSTEM AT CHICAGO MODERN PLATING: THE RINSE-LOOP SYSTEM

Chicago Modern Plating is a job shop operating 5 days a week with one 8- to 10-hour shift. There are nine plating lines with zinc cyanide plating being the principal operation. Zinc, nickel, brass, chrome, and copper are the main constituents of the approximately 378.5 liters per minute discharge.

To meet increasingly more stringent regulations, Chicago Modern investigated various treatment schemes. Conventional hydroxide precipitation systems proved to require too much area; Chicago Modern's location in a highly industrialized section of the city simply did not allow any space for a precipitation treatment system that would handle their discharge. In addition, parts of the plating shop are old, and identifying and segregating flows proved a difficult task. All wastewater does, however, enter a common main sump prior to discharge to the sewer.

Chicago Modern investigated an ion exchange system to meet their present and future pollution control needs. The system installed at the shop, however, is markedly different from any other ion exchange system used for treating industrial wastestreams in that it treats a mixed wastestream containing both heavy metals and cyanide with layers of resins in a single column. As mentioned earlier, typical ion exchange systems completely deionize wastewater, replacing cations with hydrogen ions and anions with hydroxyl ions. The system at Chicago Modern, however, uses weak- and strong-acid cation resins in the sodium form and strong-base anion resins in the hydroxyl form. The weak-acid resin is selective for cations which include toxic metals (in addition to calcium and magnesium) and exchanges its sodium ions for those in the wastewater. The anion resin removes cyanide, chromate, and other anionic metal complexes from the wastewater. It is this arrangement of resins which allows the treatment of the combined wastestream.

As a result of the sodium ion exchange mechanism, the level of dissolved solids in the effluent remains essentially unchanged from influent conditions. This water may be used in noncritical rinse applications or discharged to the sewer. If

treated water is reused in rinse applications, a portion of the water must be discharged to control the buildup of sodium salts which would result. The amount of water which may be reused, then, is dependent on water quality requirements. At present, wastewater from the ion exchange system at Chicago Modern is being discharged to the sewer because it is not suitable for rinse reuse. Eventually, the system may be able to return up to 60 percent of the treated water to the rinse tanks if it performs as intended.

From the main sump, wastewater is sent to a series of filters (Figure 18). The medium in the filters is actually used ion exchange resin although removals in the filters are physical and not chemical. This medium is intended to allow a high flow rate and very short backwashing periods. Carbon filters are not used to remove organics that might effect the ion exchange resins in this particular system. A reported advantage of contacting the strong base anion resin with a strong acid solution is that it removes any organic fouling which is a problem with strong base ion exchange resins. Backwash from the filters is sent to holding tanks then bled back to the influent. Wastewater from the filters is then pumped to the ion exchange system. Three columns are employed; at least two are always operating while a third is off-line during regeneration. This filter scheme has not worked well, causing operating difficulties discussed below in Operation and Performance.

The ion exchange columns are a mixed-bed, fixed-bed design. Other mixed-bed systems regenerate the resin by backwashing and fluidizing the anion and cation resins which separate due to different densities. The resins are regenerated independently, that is, the cation resin is regenerated with acid and the anion with caustic. The regeneration is controlled so that the acid and caustic only contact the resins they are intended to regenerate.

The system at Chicago Modern, however, avoids fluidization. A preliminary backwash is accomplished at a low flow rate to remove suspended solids. The entire bed, containing both resins, is washed with a 20 percent solution of hydrochloric acid (HCl). This removes heavy metals from the cation resin and replaces them with hydrogen ions (i.e., converts the resin to the strong-acid form). The HCl also exchanges cyanide ions on the anion resin with chloride ions.

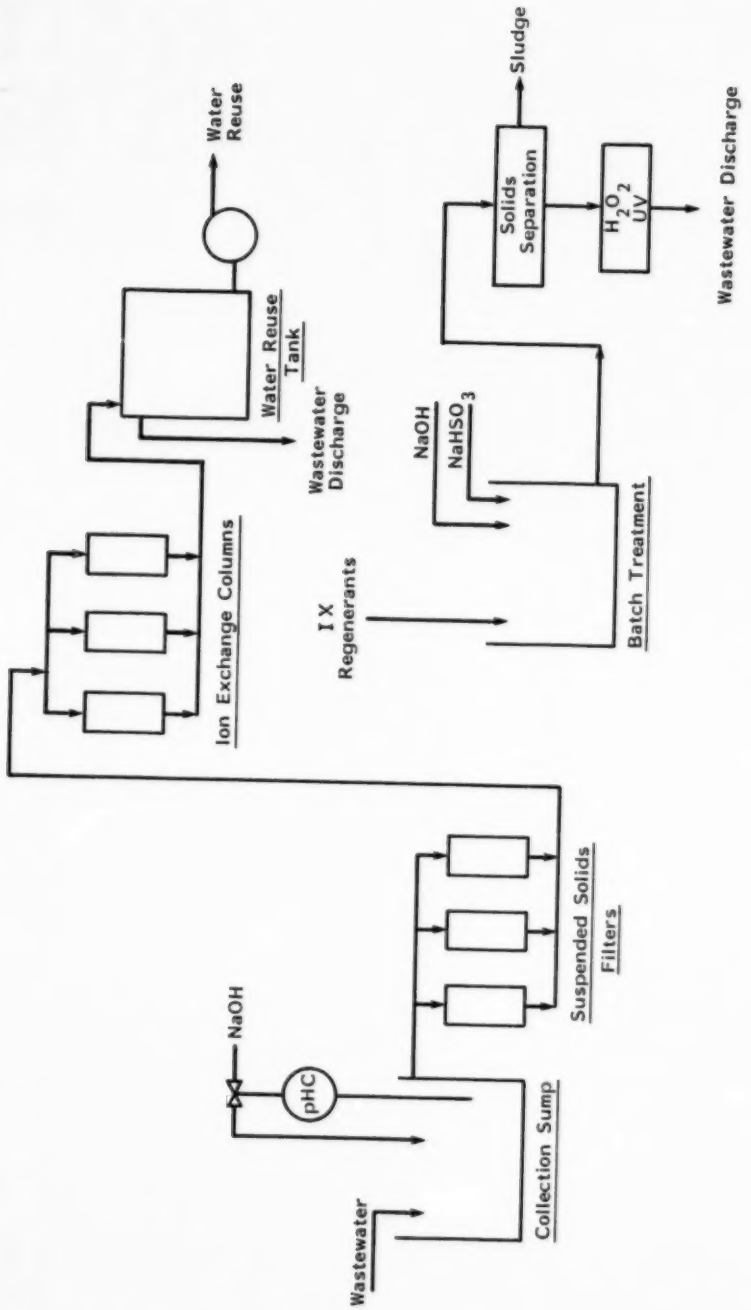

Figure 18. Rinse-Loop system

The acid regenerant is followed by a caustic rinse with 20 percent sodium hydroxide (NaOH). This now converts the cation resin to the sodium form and elutes any tightly held anions from the anion resin. The acid and caustic regenerants are each followed by a wash with fresh water and are at present both sent to a small batch treatment system for chromium reduction, cyanide destruction, clarification, and discharge. Unfortunately, this conventional treatment system malfunctions from time to time and causes problems during the sampling phase as described in the following section.

OPERATION AND PERFORMANCE

According to the manufacturer, the treatment system at Chicago Modern is still considered to be in the start-up mode.* During this start-up period, the system was not always operated according to design procedures. The most common divergence from planned operation during the sampling period was that regeneration of the ion exchange columns was not performed on schedule. Initially, all three columns with fresh resin are on-line. Each column is then meant to be regenerated approximately every 4 hours after startup of the system. During the sampling period, however, there were occasions when each column was left on-line for 11 to 12 hours; an 11-hour cycle was typical of the first 3 days of sampling. At present, there is no monitoring to determine if the resins are exhausted; the manufacturer prefers to regenerate on a schedule basis. This procedure does not make efficient use of the resin, although it would probably ensure low effluent concentrations if regeneration takes place often enough. Regeneration was not performed on the planned schedule during the sampling period because of problems with the conventional portion of the system, discussed below.

Samples were obtained, therefore, to show resin loadings after the 4-hour design period as well as after the 11-hour period typical of operation during the first 3 days of sampling. During the sampling period, no problems were encountered with the operation of the ion exchange unit and samples were obtained without interruption.

Because of cost, it was not possible to sample each column independently throughout the service cycle. The samples taken therefore represent an unoptimized configuration in terms of length of service cycle and length of backwash, regeneration, and rinse cycles. Since the samples taken represent the sum total of the three columns at single points in time, it is logical that, with optimization, significant improvements in performance could be attained.

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*The system was subsequently removed, having never achieved reliable performance (personal communication, W. Verdonk, Chicago Modern Plating, 10 June 1981).

Numerous problems with the conventional batch treatment system, however, reduced effective operating time to approximately 60 percent. Because no provisions are made to bypass a problem portion of the system, a minor problem such as a break in an air line that actuates a valve would force attendants to shut down the entire system. In general, these problems were due to poor piping design and a lack of instrumentation rather than improper application of the system. In addition, the filters, which are packed with used ion exchange resin, are reported to bleed resin during the backwash cycle. This resin then clogs the clarifier (plate settler) and leads to a sludge loaded with as much as 25 percent resin.

The treatment system at Chicago Modern is complex; it has not been established whether plant personnel will be capable of operating the system or if a full-time operator may be necessary. During this start-up period, at least one attendant is always on duty. Increased instrumentation may be a solution which would allow reduced attention.

Table 7 is a summary of the analytical results from sampling the ion exchange portion of the treatment system. Detailed results are graphed on Figures 19 through 28. The ion exchange columns performed well except when resins were allowed to become so saturated that breakthrough occurred, causing high concentrations of metals in the discharge. An apparent example of this can be seen in the first six samples for each metal. Samples 1 through 5 show consistently low concentrations of pollutants regardless of influent concentrations. However, Sample 6 (taken on Day 2) represents an on-stream time of 11 to 12 hours for the columns and shows a significant increase in effluent concentrations. After regeneration, Sample 7 once again generally shows low levels of metals and cyanide.

Specific conductivity measurements may signal resin exhaustion. Figure 26 shows several peaks in conductivity measured during the sampling period, but except for the fifth sample, these do not generally coincide with breakthroughs of metals as indicated on other graphs.

On two occasions, as indicated on Figure 28, the pH of the discharge was very high. At present there is no provision for pH adjustment of treated water from the ion exchange columns.

Table 8 shows composited metals and cyanide concentrations of the wastestream during regeneration of two columns, one regenerated on the design schedule and the other after 11 hours on-line. Column 3 results are typical of the resin loadings experienced during the sampling period and are representative

TABLE 7. SUMMARY OF SAMPLING RESULTS OF ION EXCHANGE UNIT AT CHICAGO MODERN PLATING

Parameter	Influent Range	Influent Average	Effluent Range	Effluent Average	Av. % Removal
Cyanide	25.5 - 4.4	13.63	10.0 - 1.0	3.48	74.5
Total chromium	32.2 - 2.04	11.03	24.0 - 1.30	6.40	42
Copper	2.50- 0.50	1.29	11.0 - 0.23	1.16	10.1
Nickel	13.2 - 1.60	5.45	6.25- 0.10	1.4	74.2
Zinc	46.0 -13.2	25.23	56.0 - 0.38	9.43	62.6
TSS	360 - 7.0	91.0	456 - 2.0	46.8	48.6
pH	8.6 - 3.0	6.7[a]	11.8 - 6.3	8.2[a]	-

[a]Median

Influent and effluent values, except pH, in mg/l.

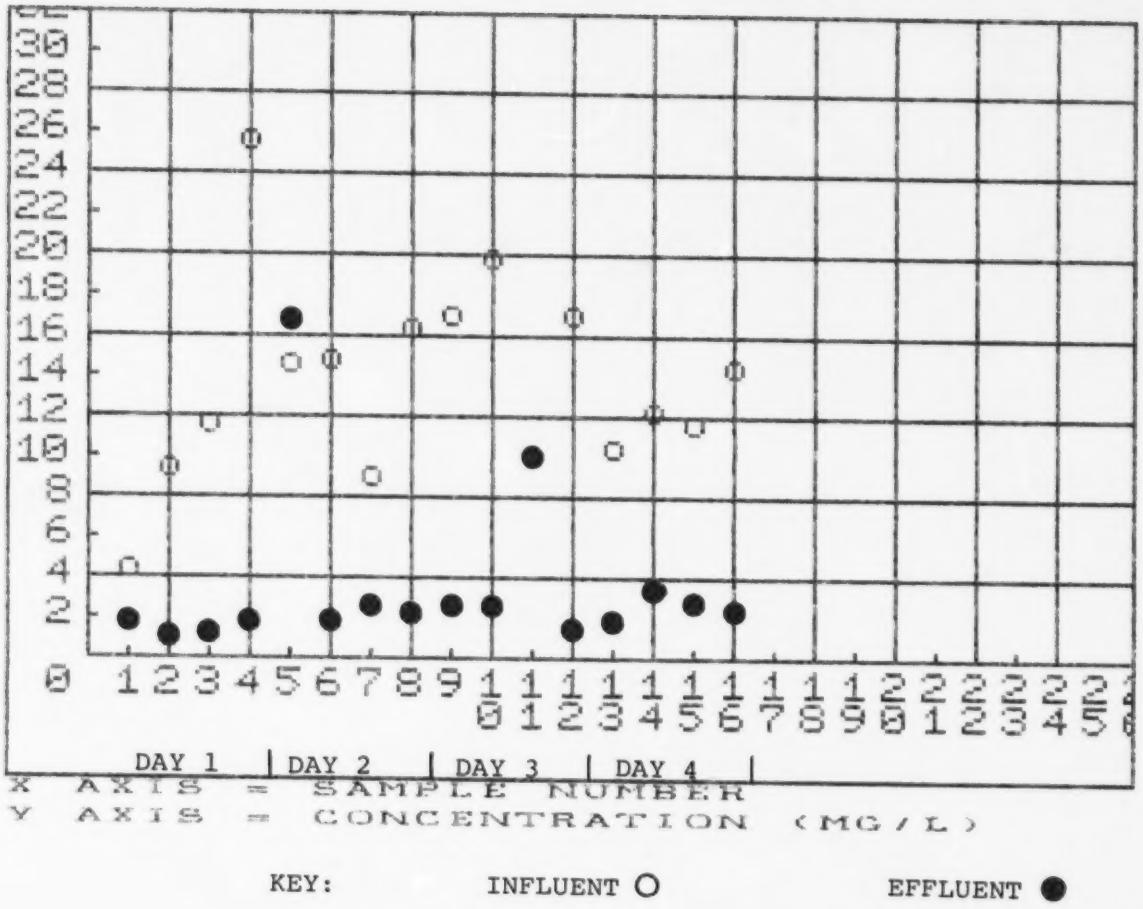


Figure 19. Chicago Modern sampling ion exchange columns - cyanide

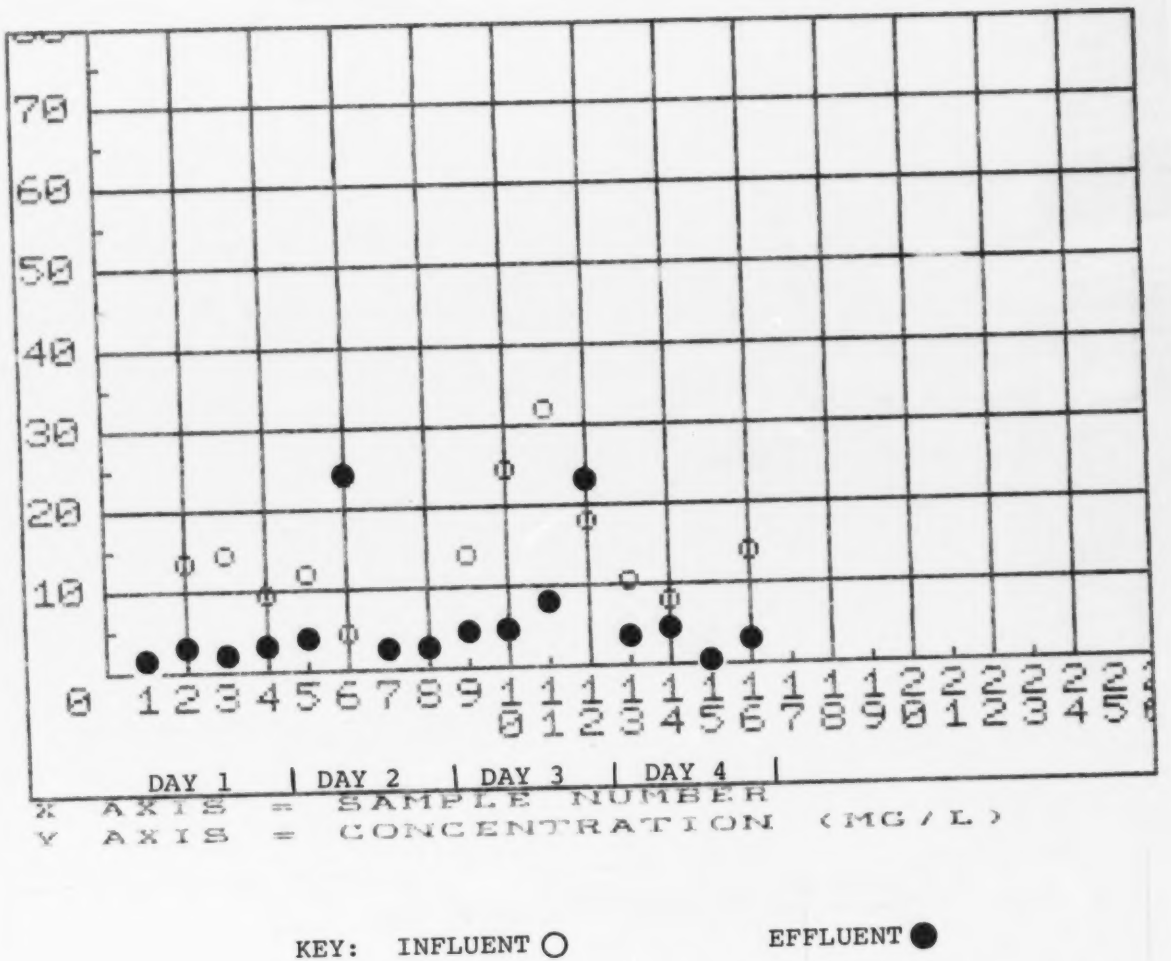

70
60
50
40
30
20
10
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26
DAY 1 | DAY 2 | DAY 3 | DAY 4
X AXIS = SAMPLE NUMBER
Y AXIS = CONCENTRATION (MG/L)
KEY: INFLUENT ○ EFFLUENT ●

Figure 20. Chicago Modern sampling ion exchange columns - total chrome

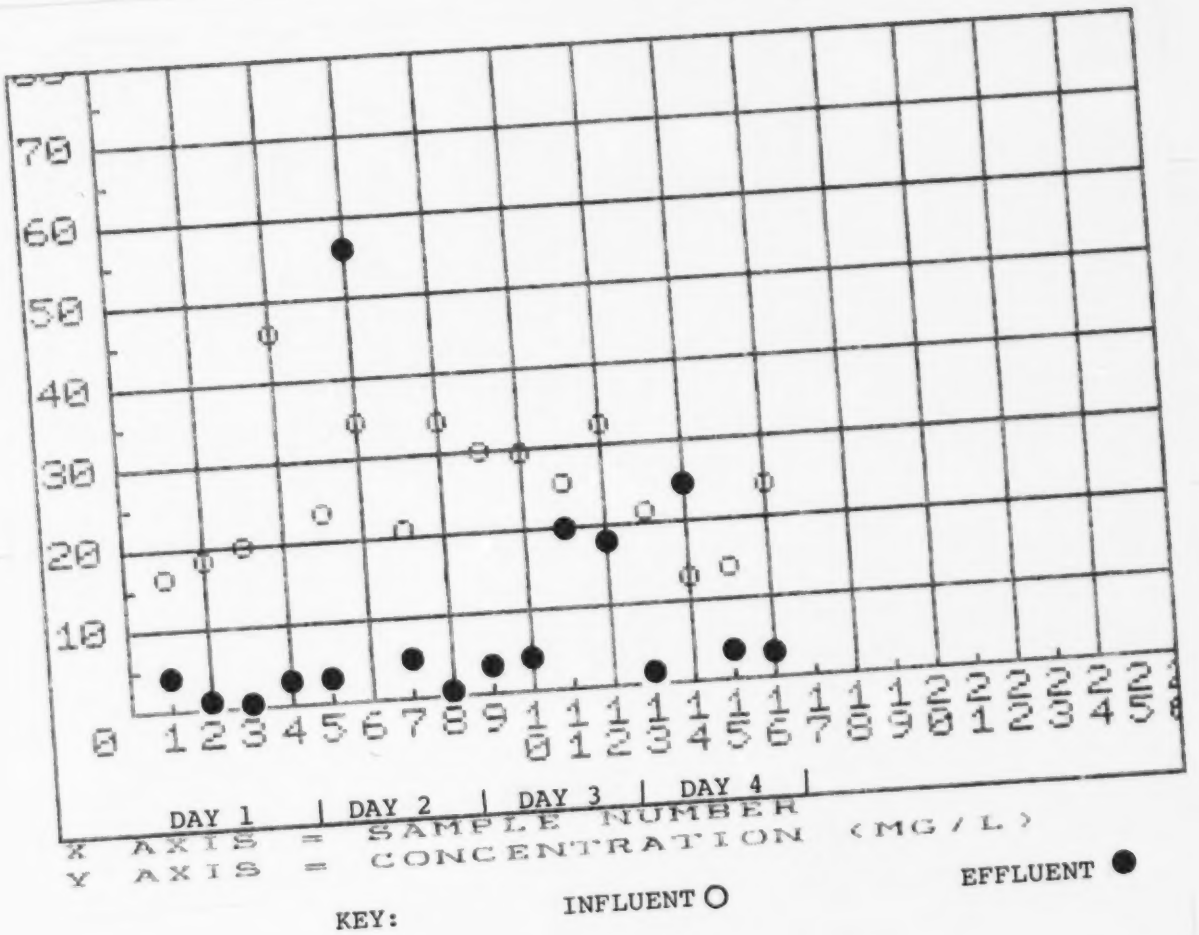


Figure 21. Chicago Modern sampling ion exchange columns - zinc

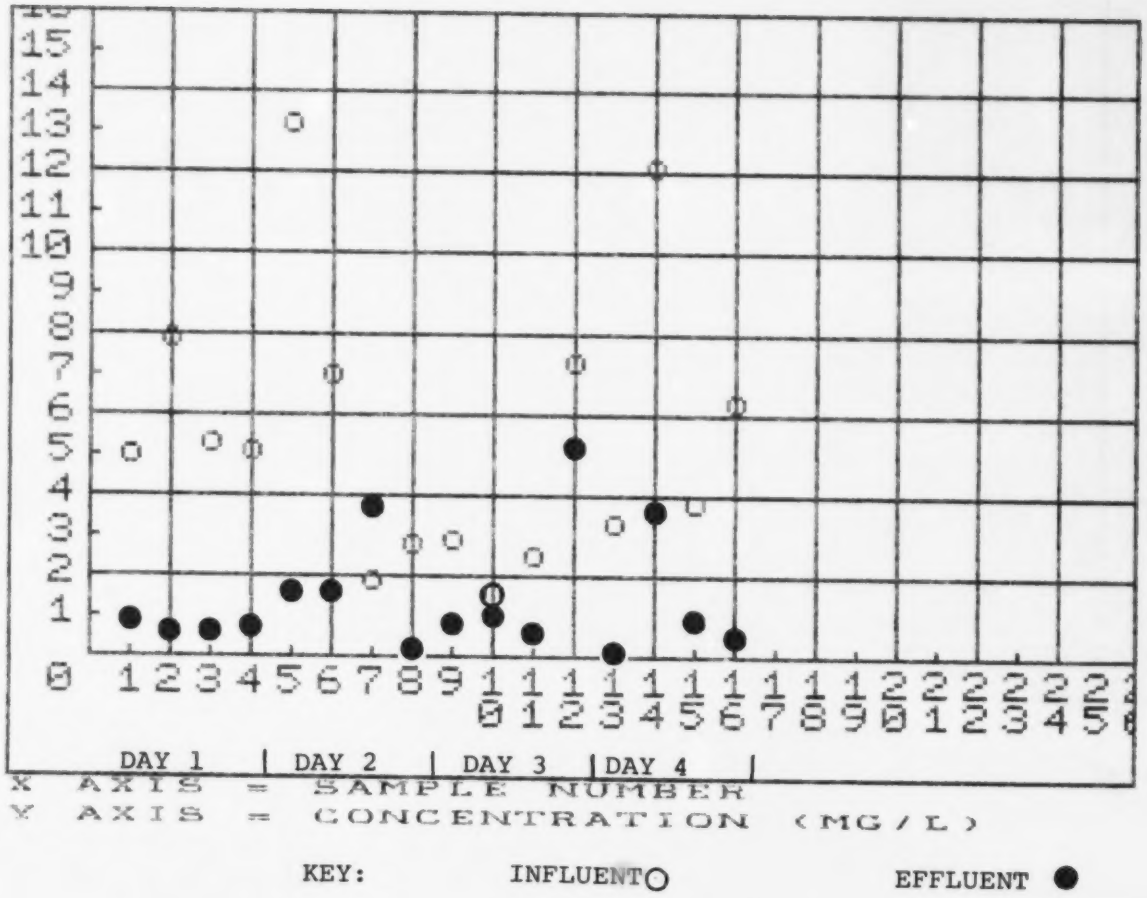


Figure 22. Chicago Modern sampling ion exchange columns - nickel

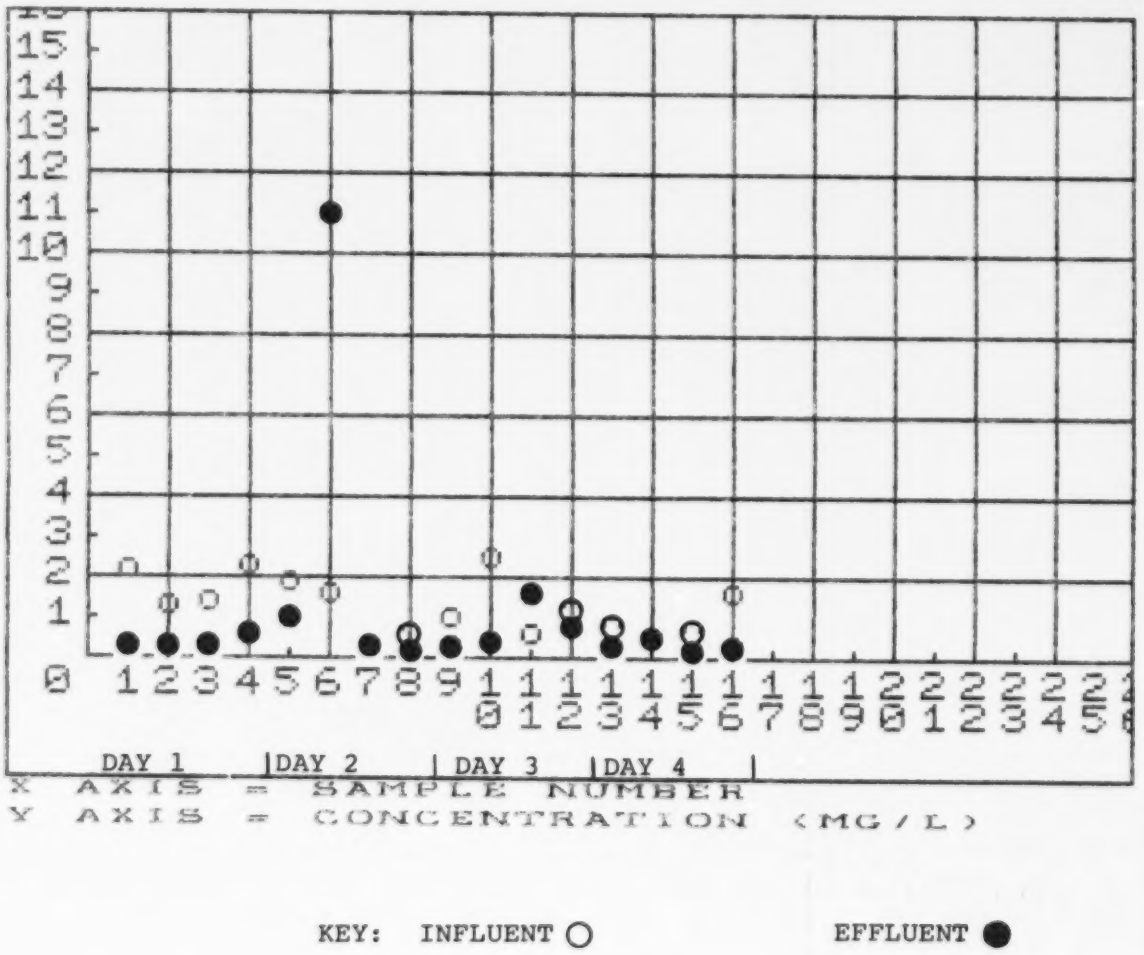


Figure 23. Chicago Modern sampling ion exchange columns - copper

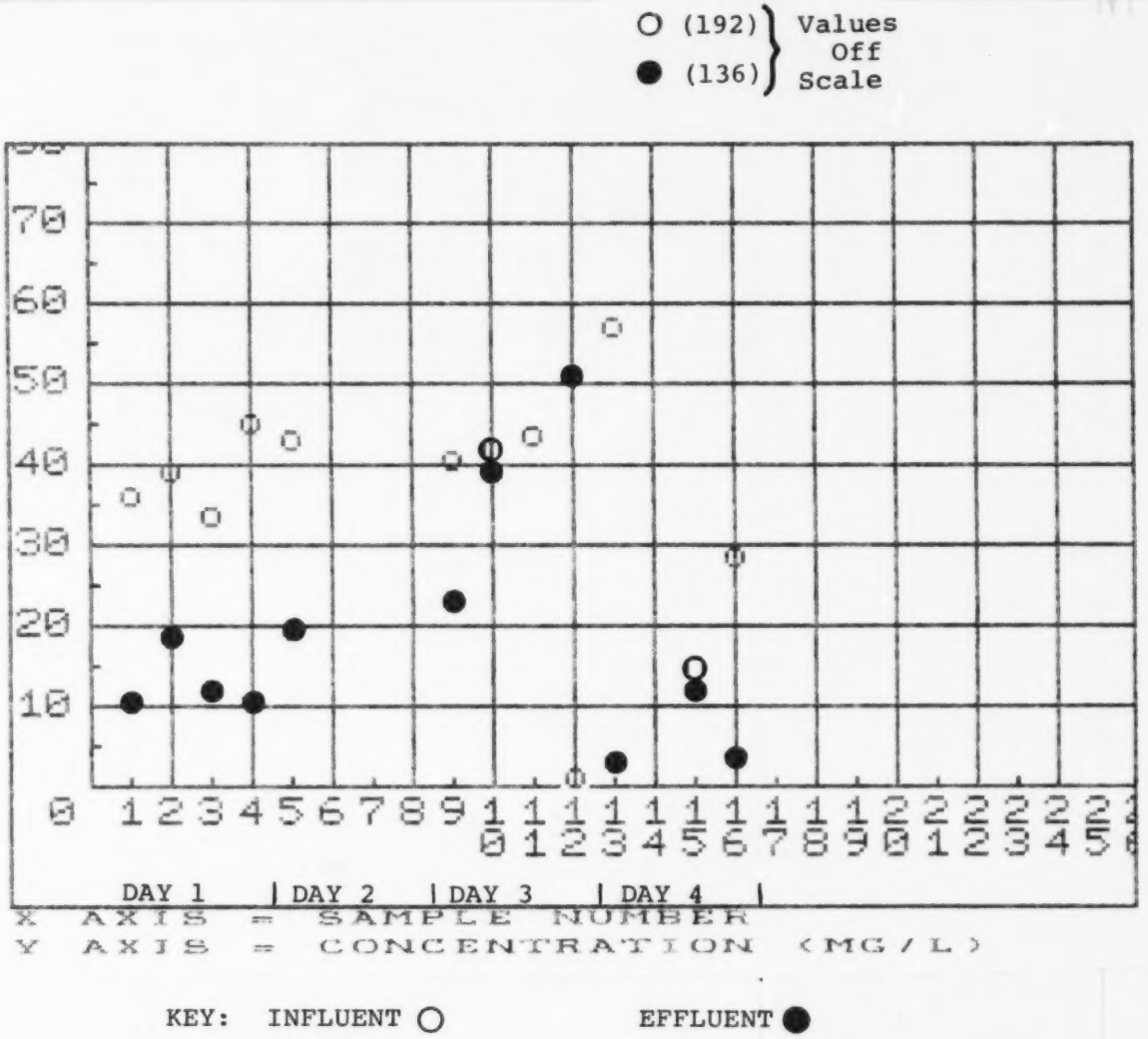


Figure 24. Chicago Modern sampling ion exchange columns - calcium

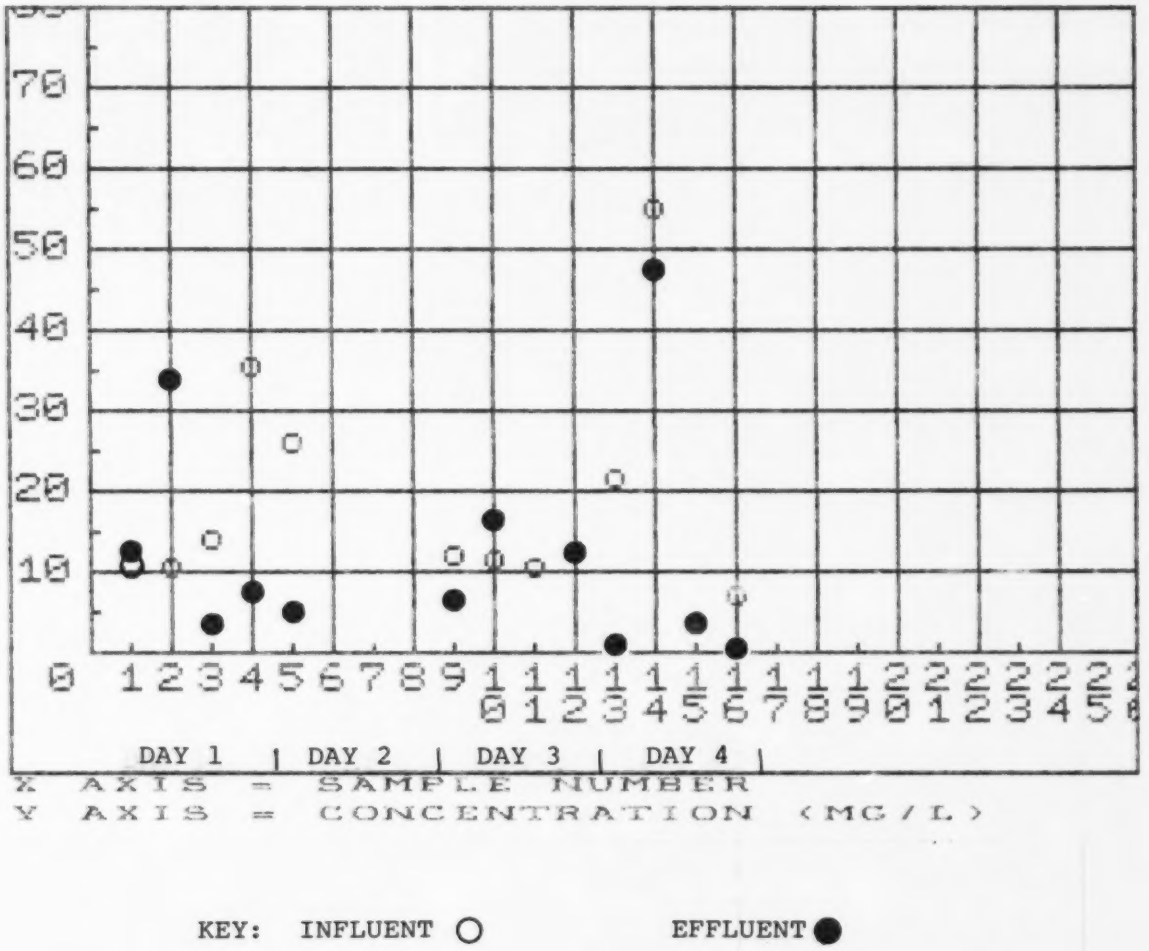


Figure 25. Chicago Modern sampling ion exchange columns - magnesium

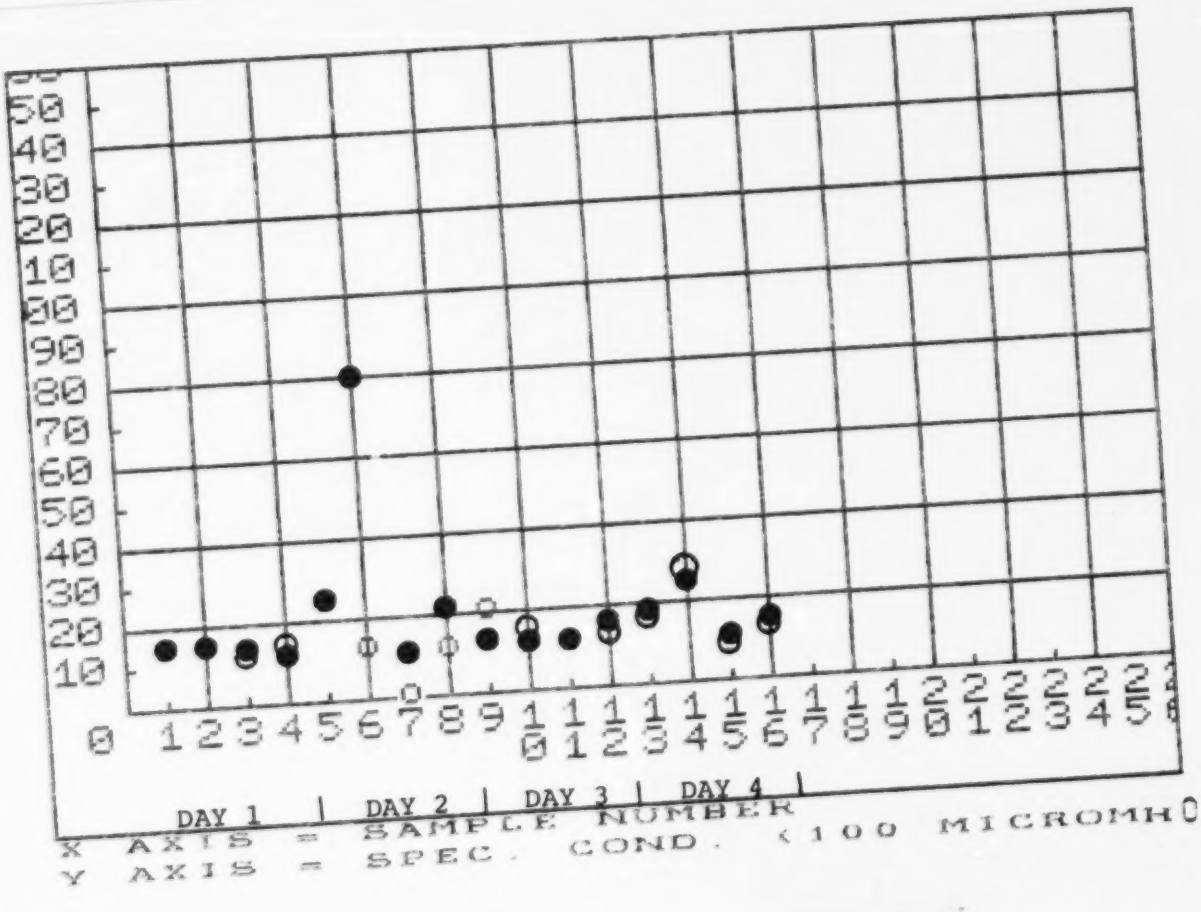


Figure 26. Chicago Modern sampling ion exchange columns - specific conductivity

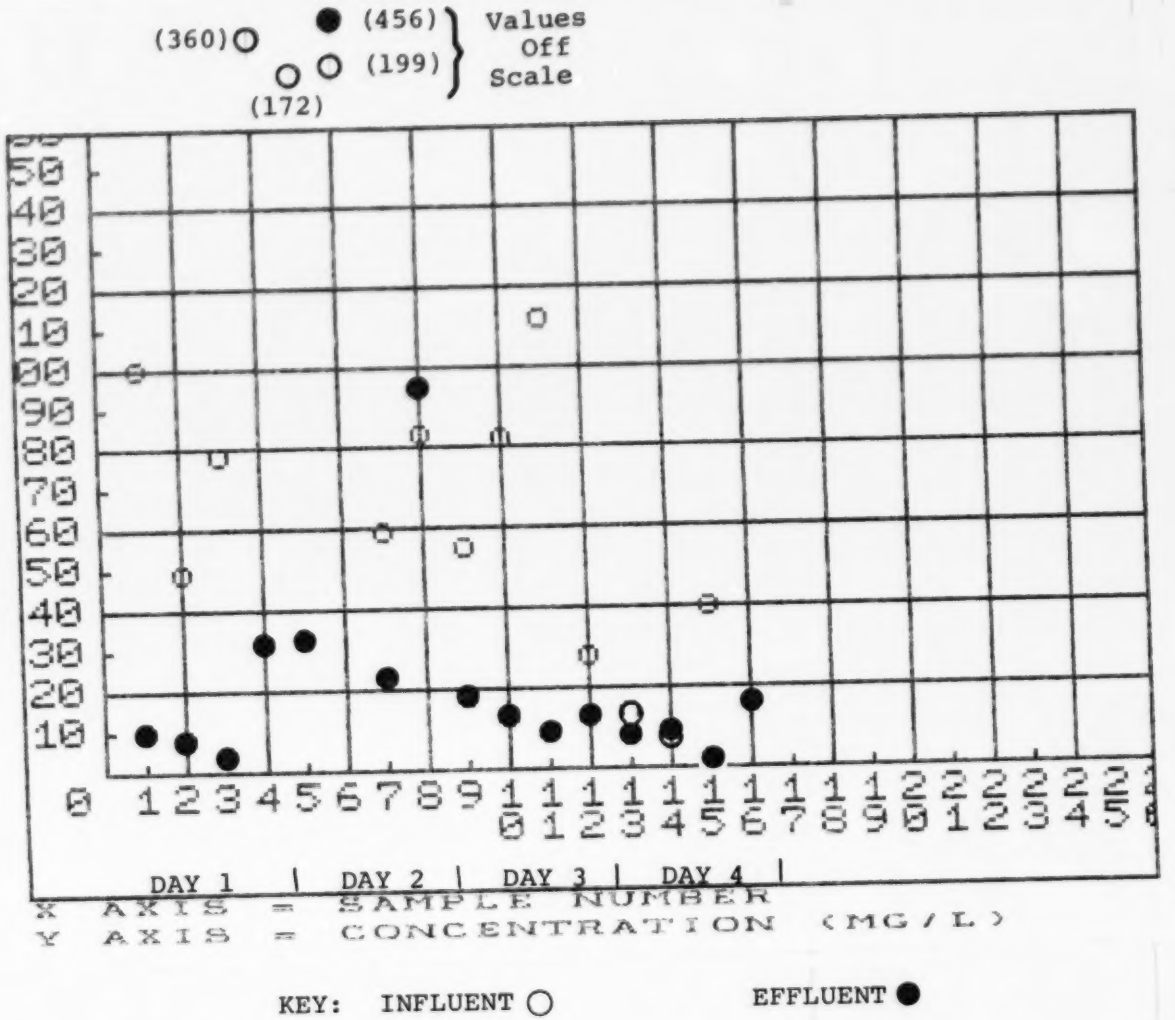
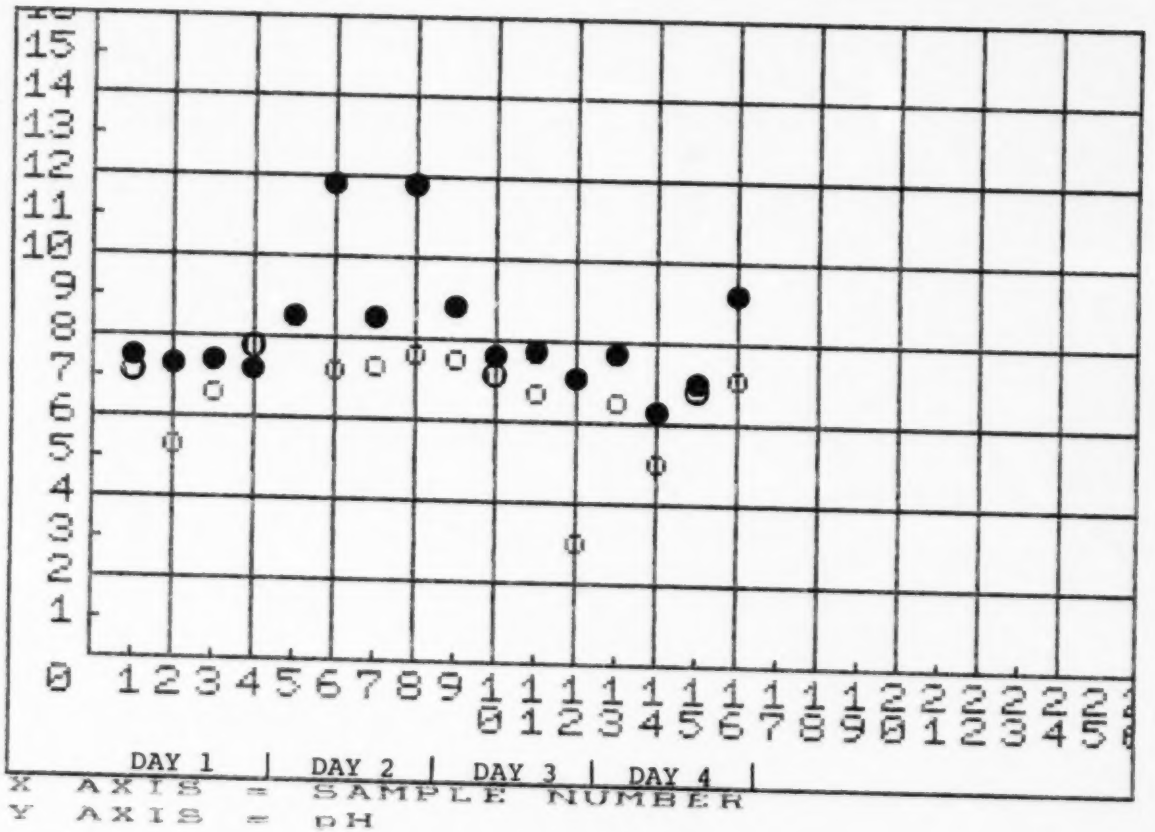


Figure 27. Chicago Modern sampling ion exchange columns - total suspended solids



KEY: INFLUENT ○ EFFLUENT ●

Figure 28. Chicago Modern sampling ion exchange columns - pH

TABLE 8. CHICAGO MODERN PLATING - COMPOSITE SAMPLES
TAKEN FROM THE WASTESTREAM DURING REGENERATION

Column	On-Stream Time (hrs)	pH	Spec. Cond. (μmhos)	Concentration (mg/l) Cn	Cr	Cu	Ni	Zn	TSS
1	4	2.52	45200	139	83.1	15.6	178	1140	923
3	11	4.51	39800	356	212	16	136	925	2350

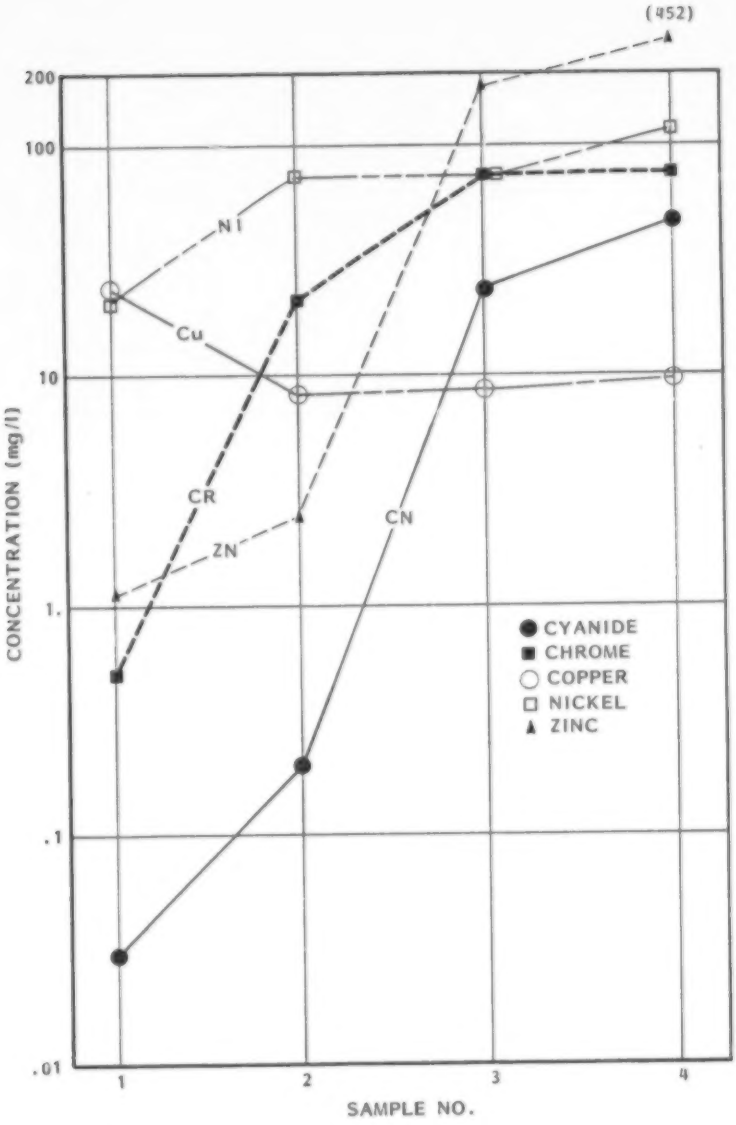
of influent concentrations to the batch treatment system. Concentrations from Column 1 are more reflective of the concentrations of metals and cyanides which will be produced once the system is operating according to specifications. This will not only have an effect on effluent quality but on costs for treatment of the regenerant stream.

Figure 29 presents analytical results from sampling of the conventional batch treatment system. Most of the operational problems existed with this portion of the system. For instance, a malfunctioning lamella-type settler was taken off-line during sampling and the wastestream was discharged with a high solids concentration. Since this treatment is a proven system, the poor performance shown in Figure 29 can be attributed to operational difficulties, including clogging by spent resin escaping the filters as discussed above. Subsequent to sampling at Chicago Modern it was learned that this clarifier was removed and replaced by a conventional large settling tank.

Some additional features of the treatment system at Chicago Modern which have not been discussed include a cyanide-complex destruction unit using ultraviolet (UV) light and hydrogen peroxide (H_2O_2). The intent is to oxidize remaining cyanide and ferro-cyanides that elude conventional treatment. This unit was sampled when operational and the results are presented in Figure 30. Very inconsistent results are indicated by exposing the treated regenerant to UV light and H_2O_2; however, this may be due to very high concentrations of cyanide (>20 and 50 mg/l in two cases) which were produced by the batch treatment system and may have reduced the effectiveness of this type of treatment. This unit was removed subsequent to the period of sampling; no equipment was added to replace its function.

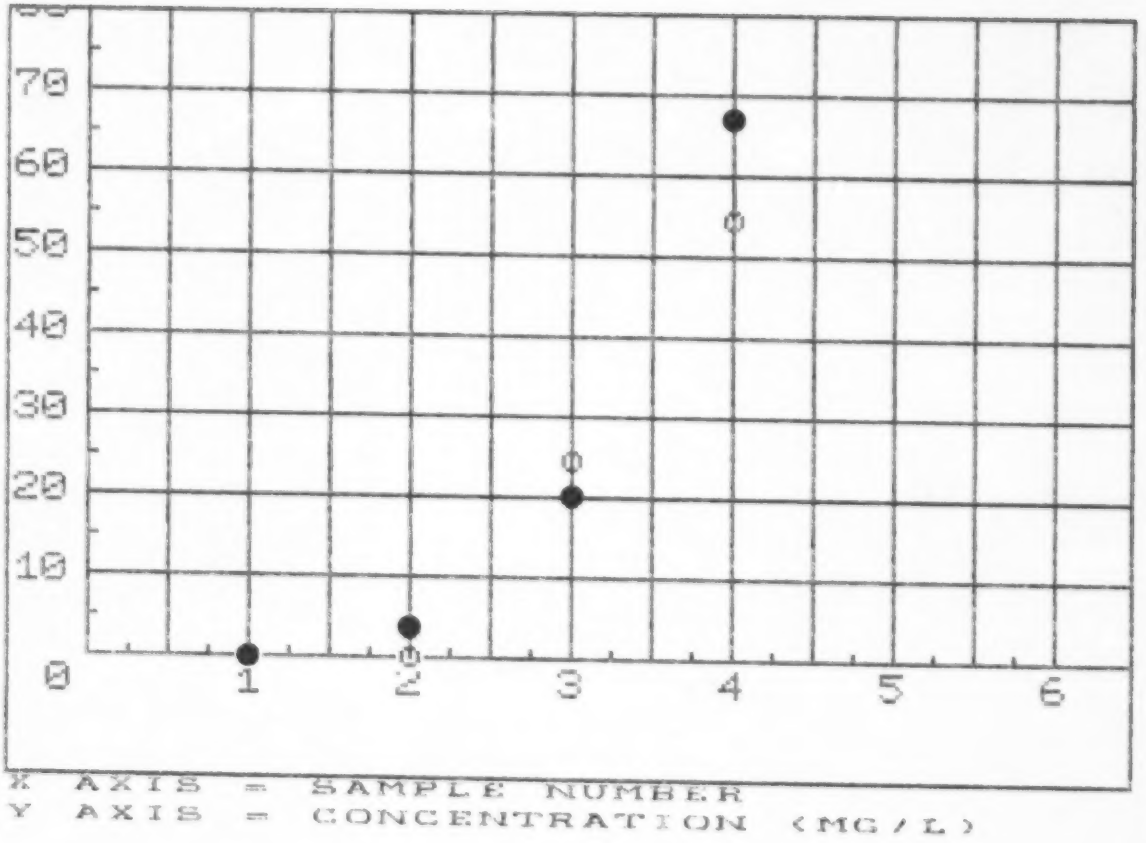
In the future, Chicago Modern plans to incorporate a cyanide recovery step. In this scheme, the acid regenerant will not go to batch treatment, but will be heated in a separate closed vessel thereby liberating hydrocyanic gas (HCN). The gas will be contacted with a sodium hydroxide solution which absorbs the HCN and produces sodium cyanide (NaCN). This solution can then be used for cyanide plating chemical makeup.

The ion exchange system at Chicago Modern was effective in reducing influent concentrations of metals and cyanides which covered a wide range of values from very dilute to moderately concentrated (from .75 kilograms per minute to 11.9 kilograms per minute of chrome, for instance). This was the case as long as operation of the system was carried out as planned. High final effluent concentrations (Figure 29) following batch



(Note: 1 sample taken each day)

Figure 29. Effluent levels from batch treatment system



KEY: INFLUENT ○ EFFLUENT ●

(Note: 1 sample taken each day)

Figure 30. Chicago Modern sampling ultraviolet light and hydrogen peroxide - cyanide

treatment of the regenerant solution (Figure 18) were due to improper column regeneration practices and equipment malfunctions during the sampling period.

COSTS

A number of interdependent factors affect the costs associated with ion exchange treatment. For example, the resin selection in turn affects regenerant dosages and subsequent waste volumes to be treated. Therefore, it is difficult to compare costs for different ion exchange systems. Table 9 presents the costs for the Rinse-Loop system at Chicago Modern based on anticipated design performance. Due to operational problems described in this report, that level of performance has not yet been achieved, leading to higher actual costs than those shown (especially for chemicals and sludge disposal). For comparison, costs also are provided for conventional treatment of the Chicago Modern wastestream. As can be seen, annualized operating costs are essentially the same within the estimate accuracy.

Reduced costs for the conventional systems would be possible by flow reduction and segregation of the wastestream, but these would require additional expenditures for engineering and inplant modifications. Reduced costs for the Rinse-Loop system are also possible since it does not at present return treated water to the plant. This would serve to reduce sewer and water fees for the ion exchange system. (In the comparison, these costs were assumed to be roughly equal and were not shown.) Another cost that would affect the Rinse-Loop system but which is not well defined at present is the cost of labor. In the example, labor has been assumed to be required for 4 hours per shift. Decreasing the labor required, however, may necessitate increased instrumentation and a higher capital cost.

TABLE 9. COST COMPARISON OF RINSE-LOOP ION EXCHANGE SYSTEM AT CHICAGO MODERN WITH CONVENTIONAL TREATMENT

Basis: 150 gpm, 2400 hrs/yr

Item	Cost	
	Conventional[a]	Ion Exchange[b]
Investment cost ($)	175,000	150,000
Annual operating cost		
Labor	4,200	8,400
Supervision	-	-
Maintenance	10,500	9,000
General plant overhead	8,345	7,150
Raw materials		
Treatment chemicals	8,285	1,300
Regenerant chemicals	-	12,725
Replacement resin	-	500
Utilities	4,000	4,000
Sludge disposal	5,664	1,990
Annual fixed costs		
Depreciation	17,500	15,000
Taxes & insurance	1,750	1,500
TOTAL ANNUALIZED OPERATING COST	$60,244	$61,565

[a]Conventional treatment includes chrome reduction, cyanide destruction, neutralization, precipitation flocculation. Costs were determined from bases used in Reference 2.

[b]Costs for maintenance, overhead and taxes and insurance were also based on Reference 2. Raw materials costs were determined from design parameters.

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2. Environmental Pollution Control Alternatives: Economics of Wastewater Treatment Alternatives for the Electroplating Industry. EPA 625/5-79-016, U.S. EPA, June 1979.

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4. Electroplating and Related Metal Finishing and Pollutant and Toxic Materials Control. Noyes Data Corporation, 1978, M. Sittig, editor.